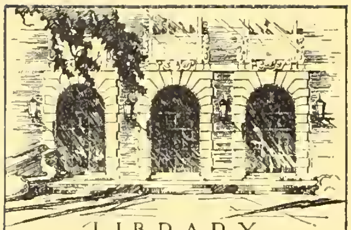

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INORGANIC SEMINARS

1952 - 1953

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COMPOUNDS CONTAINING THE SILICON-SULFUR LINKAGE

Stanley Kirschner September 30, 1952

1. Nomenclature

At a recent conference of the International Union of Pure and Applied Chemistry (5), it was decided that since the term "silicone" had been taken over as a trade name by industry, it no longer had a place in systematic nomenclature. At this same meeting a nomenclature for organo-silicon compounds was presented. It was decided that prefixes such as di- and tri- would be used to designate the number of silicon atoms present in a compound. Some examples are:

A - Silanes
  1. SiH_4 is silane.
  2. $H_3Si-SiH_3$ is disilane.

B - Silazanes
  1. $H_3Si-NH-SiH_3$ is disilazane.

C - Silthianes
  1. $H_3Si-S-SiH_3$ is disilthiane.

D - Siloxanes
  1. $H_3Si-O-SiH_3$ is dilsiloxane.

E - Hydroxy Derivatives
  1. H_3SiOH is silanol.
  2. $H_2Si(OH)_2$ is silandiol.
  3. $H_3Si-O-SiH_2OH$ is disiloxanol.

For a more comprehensive survey of organo-silicon nomenclature, the reader is referred to reference (5).

2. Historical Summary

Until as recently as ten years ago there were less than about a dozen known compounds which contained the silicon-sulfur linkage. The best characterized of these were: (a) silicon disulfide, SiS_2, which was prepared (9) by heating a mixture of silicon, carbon, and carbon disulfide; (b) silicon monosulfide, SiS, and (c) silicon oxysulfide, SiOS, which were prepared simultaneously (4,12) by heating silicon and sulfur vapor in a porcelain reaction tube; (d) silicon thiochloride, $SiSCl_2$, which was formed (2) along with SiS_2 and $SiCl_4$ by passing sulfur monochloride over crystallized silicon in a heated tube; (e) silicon thiobromide, $SiSBr_2$, which was prepared (1,11) by the reaction between $SiBr_4$ and H_2S at 150°C. with an $AlBr_3$ catalyst; (f) silicon chlorohydrosulfide, $SiCl_3SH$ (today called trichloro-thiosilanol), which was formed (11,8) by heating a mixture of $SiCl_4$ and H_2S in a porcelain tube; and (g) silicothiourea, $SiS(NH_2)_2$,

which was prepared (1) by the reaction between $SiSBr_2$ and gaseous NH_3 in anhydrous benzene; the NH_4Br produced was removed by washing with liquid ammonia.

3. Recent Developments in the Chemistry of Compounds Containing the Silicon-Sulfur Linkage

In 1950, Eaborn (6,7) described what he believed to be the first organosilicon sulfides to be reported. (However, Friedel and Ladenburg (8) described the preparation of $Si(OC_2H_5)_3SH$ in 1872). These compounds are hexaethyl- and hexamethyldisilthiane, which were prepared as products in a conversion series developed by Eaborn. The series is:

$$R_3SiI \rightarrow (R_3Si)_2S \rightarrow R_3SiBr \rightarrow (R_3SiH) \rightarrow \left\{\begin{matrix} R_3SiNC \\ R_3SiCl \end{matrix}\right\} \rightarrow R_3SiNCS \rightarrow R_3SiNCO \rightarrow \left\{\begin{matrix} (R_3Si)_2O \\ R_3SiF \end{matrix}\right\}$$

Any compound in the series may be converted to any other on its right by heating with the appropriate silver salt. The yields are frequently better than 90%, and the reverse conversions do not seem to occur. For example, the hexa-alkyldisilthianes were prepared by heating the corresponding trialkyliodosilane with Ag_2S.

Eaborn states that the silthianes are the sulfur analogues of the siloxanes, but they are (a) less stable (thermally) than the siloxanes, and (b) completely hydrolyzed when brought into solution. He feels that this is due largely to a weaker bond between silicon and sulfur than between silicon and oxygen, and he cites the values for the heats of formation of the Si-S bond and the Si-O bond given in Sidgwick (13) in support of his ideas:

Heats of Formation of Links from Atoms (H_a)

Si-O	89.3 kcal/mole
Si-S	60.9 kcal/mole

However, Eaborn prepared these disilthianes from trialkyliodosilanes, and, according to Larsson and Marin (10), these are rather difficult to obtain. They, therefore, devised a method for the preparation of hexaethyldisilthiane which does not involve any of the iodosilanes. They report that, after passing H_2S through $(C_2H_5)_3SiNH_2$ (163 grams) for several hours, they obtained 34.5 g of $(C_2H_5)_3SiSH$ and 95.2 g of $(C_2H_5)_3Si\text{-}S\text{-}Si(C_2H_5)_3$. In addition, they found that similar treatment on tri-n-propylaminosilane gave tri-n-propylthiosilanol and hexa-n-propyldisilthiane. The methyl derivatives were not prepared because the authors were unable to prepare the starting material, trimethylaminosilane.

Champetier, Etienne, and Kullman (3) continued the study of silicon-sulfur compounds and have recently described the preparation of some silanthiols and "thiosilicones". Although Friedel and Ladenburg (8) had been able to prepare trichlorothiosilanol by heating $SiCl_4$ and H_2S above 600°, a method utilizing so high a temperature could not be used in the preparation of organo-silicon compounds, so the authors reacted alkali and alkaline earth hydrosulfides with alkylhalosilanes to prepare the alkylthiosilanols. For example, the authors reacted H_2S with a Grignard Reagent to get a magnesium hydrosulfide:

$$2H_2S + 2RMgX \rightarrow (HS)_2Mg{\cdot}MgX_2 + 2RH$$

which was reacted with the triethylhalosilane $(C_2H_5)_3SiY$. The products were $(C_2H_5)_3SiX$ (when the halogen Y was classified before the halogen X in the series F, Cl, Br, I) and hexaethyldisilthiane:

1. $2(C_2H_5)_3SiY + MgX_2 \rightarrow 2(C_2H_5)_3SiX + MgY_2$
2. $\left\{\begin{matrix}2(C_2H_5)_3SiX\\ 2(C_2H_5)_3SiY\end{matrix}\right\}\text{or} + Mg(SH)_2 \rightarrow 2(C_2H_5)_3SiSH + \left\{\begin{matrix}MgX_2 & \text{or}\\ MgY_2 & \end{matrix}\right\}$
3. $2(C_2H_5)_3SiSH \rightarrow (C_2H_5)_3Si{-}S{-}Si(C_2H_5)_3 + H_2S$

In order to obtain trimethylthiosilanol with only a small percentage of the hexamethyldisilthiane, LiSH was used in place of a magnesium compound:

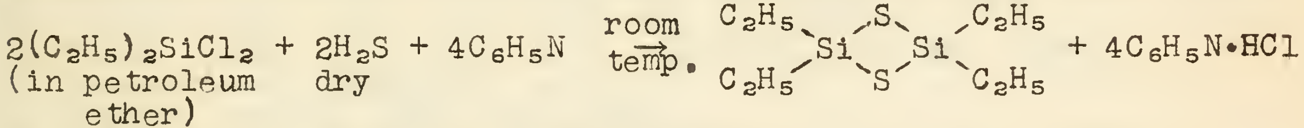
$$LiR + H_2S \xrightarrow[C_6H_5CH_3]{dry} LiSH + RH$$

When 0.75 moles of LiSH was treated with 0.5 moles of trimethylchlorosilane at room temperature, a 48% yield of $(CH_3)_3SiSH$ and only a small quantity of hexamethyldisilthiane were obtained upon fractional distillation.

These authors also report that a convenient way to obtain a high yield of various disilthianes is to react an alkylhalosilane with H_2S in the presence of pyridine:

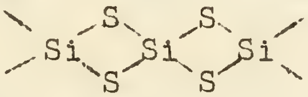
$$2(C_2H_5)_3SiCl + H_2S + 2C_6H_5N \rightarrow (C_2H_5)_3Si{-}S{-}Si(C_2H_5)_3 + 2C_6H_4N{\cdot}HCl$$

Diethyldichlorosilane leads to tetraethylcyclodisilthiane:

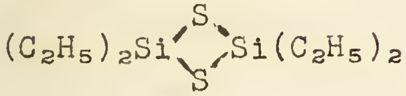


$2(C_2H_5)_2SiCl_2$ (in petroleum ether) + $2H_2S$ dry + $4C_6H_5N$ $\xrightarrow{\text{room temp.}}$ + $4C_6H_5N{\cdot}HCl$

in a 78% yield, which the authors claim is the first example of a "thiosilicone", and which is similar in structure to silicon disulfide:



A great deal of additional investigation remains to be carried out in the field of silicon-sulfur chemistry, as can be seen from the following tabulation of the few silicon-sulfur compounds which have been reported. Even these have not been studied to any great extent, and they should be investigated further.

Compound	Melting Point °C.	Boiling Point°C.	Reference
SiS_2	Subl.	White Heat	9
SiS		Subl. at 940 (20 mm.)	4
$SiOS$			4
$SiSCl_2$	75	185	2
$SiSBr_2$	93	150 at (18.3 mm.)	1
$SiCl_3SH$		96 - 100	11
$SiS(NH_2)_2$			1
$[(C_2H_5)_3Si]_2S$		278-279 at (750 mm.)	6,3
$[(CH_3)_3Si]_2S$		163-164	3
$Si(OC_2H_5)_3SH$		164	8
$(C_2H_5)_3SiSH$		158	10
$(CH_3)_3SiSH$		77-78	3
$(n\text{-}C_3H_7)_3SiSH$		83-84 at (7 mm.)	10
$[(n\text{-}C_3H_7)_3Si]_2S$		168 at (7 mm.)	10
		160 - 162	3

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ANALYTICAL PROCEDURES USING ACETIC ACID AS A SOLVENT

Donald H. Wilkins   October 7, 1952

INTRODUCTION

Acid-base relationships in nonaqueous solvents were first defined by Franklin in 1905 (1) and later extended by Germann in 1925 (2). Although the literature on nonaqueous solvents dates back nearly fifty years, the practical use of these solvents in analytical procedures is covered only in the more recent publications. Acid-base titrations in nonaqueous solvents are particularly useful. They may be performed with simple techniques and without elaborate equipment. The procedures are accurate and rapid. Many organic compounds which are too weakly acidic or basic act as relatively strong acids and bases in appropriate nonaqueous solvents. Acetic acid, an acid solvent, is useful for titrating many organic bases which are either only slightly soluble in water or too weakly basic to give sharp end points. Most aromatic, aliphatic, and heterocyclic amines may be titrated as bases in acetic acid.

DISCUSSION

Kolthoff and Williams (3) studied the order of acidity of several acids in acetic acid. They found: $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$. Of these acids, perchloric is the most suitable titrant. It is the strongest acid, has fewer insoluble salts, and has only one replaceable hydrogen ion. Hydrochloric acid has a high escape velocity; a 1.0 N solution of hydrochloric acid in acetic acid fumes about the same as 16 N solution in water. Sulfuric acid does not always act as a monobasic in its reactions.

Many salts which do not change the reaction of water undergo solvolysis in acetic acid (4). The acidity of potassium salts of the following inorganic acids decreases in the order $ClO_4^- > I^- > Br^- > Cl^- > NO_3^-$.

Salts having a common ion show decreasing acidity in the order Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++} > (Ag^{+}) > Li^{+} > Na^{+} > NH_4^{+} > K^{+} > Rb^{+}.

Water interferes with the end point of the titrations of bases in acetic acid and consequently should be removed. The water introduced in making up the titrant by dissolving 70 to 72 per cent perchloric acid in glacial acetic acid is removed by adding the calculated amount of acetic anhydride. The coefficient of cubic expansion is large enough for acetic acid so that an accurate temperature control is necessary. The temperature of the titrant should be the same for the standardization and the titration of the unknown; otherwise a correction must be made for volume changes. For precise research work weight burets are recommended.

With volume burets the accuracy of titrations in acetic acid is of the same order as aqueou titrations (0.2%).

DETERMINATION OF THE END POINT

A. Potentiometric titrations

Conant and Hall (5) suggested the use of a saturated chloranil electrode (tetrachloroquinone and its hydroquinone). Its advantages are chemical inertness and low solubility. Theoretically the dependability of the chloranil electrode depends on the solution being at equilbrium with both the solid quinone and the hydroquinone. The solution to be titrated is saturated by adding an excess of the solids and stirring for ten minutes at 25°, the working temperature. If a volume of titrating solution is now added an unsaturation occurs. This is not important if the volume added is small compared to the total volume of solution. This is to be expected unless there is a large difference in the rate of solution of two solids.

The reference electrode was a saturated calomel electrode which was connected to a beaker of saturated potassium chloride by a siphon filled with saturated potassium chloride. The chloranil electrode

was connected to the beaker of saturated potassium chloride by a siphon filled with a supersaturated solution of lithium chloride in acetic acid which was prevented from crystallizing by dissolving a small amount of gelatin in the acetic acid. The amounts of gelatin and lithium chloride may be varied over wide limits without appreciable changes in the performance of the bridge. For special purposes the siphon from the reference electrode was stoppered with glass and dipped directly into the solution to be titrated.

The e.m.f. was measured with a potentiometer and a quadrant electrometer.

Fritz (6) used a glass electrode as an indicator electrode and a silver wire with a thin coating of silver chloride as a reference electrode. A Beckman Model G pH meter was used to determine the potential. This system eliminates the salt bridge since the silver electrode may be immersed in the solution to be titrated.

The titration curves are obtained by a plot of e.m.f. vs. ml. of reagent added. The curves are comparable in shape to those obtained in aqueous solutions. The end point may be taken directly from the curve but is more accurately determined by plotting $\Delta E/\Delta V$ vs. ml. of reagent added.

B. Visual titrations

Nadeau and Branchen (7) found that crystal violet, α-naphtholbenzein and benzoylauramine are suitable indicators for the titration of bases in acetic acid. The acid and alkaline colors of the indicators are given in table I.

These indicators, however, do not give simple color changes. The color is dependent on the ionic strength of the solution as well as the pH . Accurate results may be obtained by first titrating potentiometrically with the indicator present to determine the proper color at the end point. Subsequent determinations are made by tit-

rating to the same color using a standard for comparison. The indicators are 0.1% solutions in acetic acid or chlorobenzene.

TABLE I

Indicator	Acid color	Alkaline color
methyl violet	green	v.a
crystal violet	green	blue
α-naphthol-benzein	green	yellow
benzoyl auramine	yellowish	blue-green

To prepare a 0.1 N perchloric acid solution in acetic acid mix 8.5 ml. of 72% perchloric acid with 200 to 300 ml. of glacial acetic acid and add 20 ml. of acetic anhydride. Dilute to 1 liter with glacial acetic acid and allow to stand overnight to permit complete reaction of the acetic with the water present.

The perchloric acid is standardized against potassium acid phthalate which has been used as primary standard acid in aqueous solutions and is now finding use as a primary standard base in acetic acid. About 0.5 gms. of potassium acid phthalate is accurately weighed and added to 60 ml. of glacial acetic acid. The mixture is refluxed gently to dissolve the salt. After cooling methyl violet (0.1% in chlorobenzene) is added and the solution titrated with perchloric acid. The precipitate of potassium perchlorate does not interfere with the end point.

To prepare 0.1 N perchloric acid in dioxane dissolve 8.5 ml. of 77% perchloric acid in 1 liter of dioxane. Standardize with potassium acid phthalate as described above.

A 0.1 N solution of sodium acetate may be prepared by dissolving 8.2 gms. of anhydrous sodium acetate in glacial acetic acid and diluting to 1 liter with acetic acid. The solution is standardized against a standard perchloric acid solution.

Amino acids (7,8)

Acids which have an acid ionization constant of 10^{-5} or less in

aqueous solution are neutral in acetic acid. Consequently amino acids may be titrated as bases. The sample is dissolved in exactly 50 ml. of 0.1 N perchloric acid. Two drops of methyl violet indicator are added and the excess acid back-titrated with 0.1 N sodium acetate.

Amines (8-13)

A sample containing two to four equivalents is dissolved in 50 ml. of acetic acid. Add two drops of methyl violet and titrate with 0.1 N perchloric acid to the first disappearance of the violet color. The end point may be determined potentiometrically in the presence of highly colored compounds which do not give a sharp end point. Micro quantities of amines may be titrated with 0.001 N perchloric acid. Most aliphatic and aromatic amines can be titrated unless they are heavily substituted with halogens, nitro, aldehyde or other negative groups.

Wagner, Brown, and Peters (14) have proposed a procedure for differentiating between primary, secondary and tertiary amines. Tertiary amines are determined first by treating the sample with 20 ml. of acetic anhydride and 2 ml. of acetic acid and allowing the solution to stand for three hours. Primary and secondary amines are converted to almost neutral acetylation products. Thirty ml. of acetic acid is added and the solution titrated potentiometrically with perchloric acid. Primary amines react with salicylaldehyde to form Schiff bases which are weaker than the primary amine. By titrating aliquots of the sample it is possible to determine all three amines in a mixture.

Salts (8,9,15,16)

Salts of weak carboxylic acid react with a strong acid according to the following equation;

$$NaA + H^+ \longrightarrow Na^+ + HA$$

If the acid HA is sufficiently weak the salt may be titrated quantitatively. This procedure has been applied to the salts of a few weak acids in aqueous solution. In an acid solvent, such as acetic acid, the number of salts which may be titrated is considerably larger. The alkali salts of most carboxylic acids and some inorganic acids can be titrated in acetic acid.

Pefer and Wollish (15) have introduced a method for titrating halide acid salts of organic bases. Mercuric acetate binds the halogen anions without affecting the titration of the base portion of the salt with perchloric acid. The reaction is believed to proceed as follows:

$$\text{Organic base}\begin{bmatrix}HI\\HBr\\HCl\end{bmatrix}\xrightarrow[HgAc_2]{\text{excess}}\begin{matrix}\text{acetate of}\\\text{organic base}\end{matrix}+\begin{bmatrix}HgI_2\\HgBr_2\\HgCl_2\end{bmatrix}$$

$$\xrightarrow[\text{(std)}]{HClO_4}\ \begin{matrix}\text{perchlorate of}\\\uparrow\text{organic base}\end{matrix} + HAc$$

$$\text{voltage change}$$

The weighed sample is dissolved in 8 ml. acetic acid. If the salt is an acid halide of an organic base, add 10 ml. of mercuric acetate (6 gms/100 cc. HAc), titrate with perchloric acid using the potentiometric method to determine the end point.

CONCLUSION

The use of nonaqueous solvents such as acetic acid eliminates many tedious analytical procedures. The applications in industrial work are extensive ; however, the theoretical background for many of these procedures has not been developed as much as might be desired. There is a need for considerable research to develop suitable indicators and electrode systems. There are over five hundred acid-base indicators available but only a few can be used in acidic solvents such as acetic acid. Indicators with different transition ranges should be available for the entire transition range.

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THE SOLVENT PHOSPHORYL CHLORIDE, $POCl_3$

S. J. Gill October 14, 1952

INTRODUCTION

The interest in non-protonic solvents has been stimulated within recent years both from a practical and a theoretical point of view. The properties of a particular solvent have a marked influence upon various compounds with regard to solubility, ionization, reactions, and the possibilities of unique syntheses. Thus non-protonic solvents find a special place by providing liquid media which are devoid of hydrogen. Theoretical explanation of such systems has extended and verified acid-base concepts. Experimental work with non-protonic solvents necessitates a more accurate description of solubility phenomena, suggests some of the physical properties involved, and provides a possible means for clarification of liquid state reactions. Phosphoryl chloride suggests practical as well as theoretical utility as a non-protonic solvent.

PROPERTIES

Some of the physical properties of phosphoryl chloride are listed in the following table:

Table 1

Molecular weight	153.39	
Melting point, °C	1.25	
Boiling point, °C	105.8	
Critical temperature, °C	329	(2)
Density, g/cc	1.645 (25°C)	(1)
Molec. volume, cc/mole	101.85 (105.8°C)	(1)
Specific conductivity, 25°C	$1.7 \times 10^{-6} ohm^{-1} cm^{-1}$ (3) 1.63×10^{-6}	(1)
Dielectric constant	13.9 (22°C)	(4)
Cryoscopic constant	76.8	(5)
Ebullioscopic constant	54.7	(6)
Surface tension, dyne/cm	31.9 (18°C)	(3)
Heat of vaporization kcal/Mol	8.06	(6)
Heat of fusion kcal/Mol	3.07	(5)
Troutons constant cal/degree	21.3	
Heat of formation (liquid) kcal/Mol	146	(7)
Kinematic viscosity, centistokes	0.669	(1)

A less extensive list of properties of other non-protonic solvent materials is given in Table 2 (8).

Table 2

Solvent	Melting Point	Boiling Point	Molecular Volume mol/cc	Dielectric Constant	Dipol-moment	Specific Conductivity $ohm^{-1}\ cm^{-1}$
SO_2	-75.7	-10.02	44 (-10°)	13.8 (15°)	1.60	1×10^{-7} (0°)
N_2O_4	-11.3	21.1	61.7 (20°)	2.42 (18°)	0.4	1.3×10^{-12} (17°)
$NOCl$	-61.5	-6.5		18.2 (12°)		2.9×10^{-6} (20°)
$COCl_2$	-126	8	69.2 (0°)	4.73 (0°)	1.18	7×10^{-9} (25°)
$SeOCl_2$	9.8	178	68.5 (20°)	46.2 (20°)	2.62	2×10^{-5} (25°)
$SOCl_2$	-104.5	75.7	72.5 (20°)	9.05 (22°)	1.58	1×10^{-8} (20°)
I_2	113.6	183	68.5 (183°)	11.1 (118°)	0	9×10^{-6} (140°)
BrF_3	9	127	48.2 (9°)			8×10^{-3} (25°)
IF_5	8	97	63.5 (20°)			1.5×10^{-5} (25°)
ICl	27.2	97.4	52.3 (29°)			4.5×10^{-3} (35°)
IBr	40	119	55.0 (42°)			3×10^{-4} (40°)
AsF_3	-8.5	63	48.8 (20°)		2.6	2.3×10^{-5} (25°)
$AsCl_3$	-18	130.2	84.0 (20°)	12.8 (20°)	2.1	1.4×10^{-7} (0°)
$HgBr_2$	238	320	74.4 (320°)	9.84	0	1.5×10^{-4} (242°)

Phosphoryl chloride resembles water in liquid range and low self-ionization. Its dielectric constant is greater than that for SO_2. The relatively large molecular volume is worthy of note. The dipole moment of the P-O bond has been calculated as 3.5 (9). Molecular weight determinations in benzene give values from 153'4 to 166, thus showing slight if any association (10).

PREPARATION OF WATER-FREE $POCL_3$

Commercial $POCl_3$ is readily available and costs from 13 to 15 cents a pound (11). The methods or production are: a) heating a mixture of P_2O_5 and PCl_5, or b) passing chlorine over calcium phosphate and charcoal at 750°C (12).

Purification for solvent use requires the elimination of all traces of water. Water reacts with phosphoryl chloride to give phosphoric acid and hydrogen chloride, thereby raising the conductivity of the solvent. Walden (3) treated the material with P_2O_5 and distilled the dry $POCl_3$ from the resulting phosphoric acid. However this does not eliminate the hydrogen chloride. To do so Cady and Taft (13) added metallic sodium and distilled the resulting mixture at atmospheric pressure. This technique occasionally results in explosion.

In order to minimize the possibility of explosion Gutmann (1) employed the following procedure: the commerical product was first distilled using a 30 cm. column ground glass apparatus; sodium was added to the distillate and carefully refluxed; after cooling, the material was distilled twice under high vacuum. Explosion does not occur under these conditions.

CONDUCTIVITY AND SOLUBILITY STUDIES

The specific conductivity of phosphoryl chloride passes through a maximum at 88°C. Over the same temperature range both the density and viscosity decrease monotonically. A possible explanation (1) of this phenomenon is given by considering the following equation:

$$POCl_3 \quad = \quad POCl_2^{+} \; + \; Cl^{-}$$

$$\text{or} \qquad 2POCl_3 \quad = \quad POCl_2^{+} \qquad POCl_4^{-}$$

These ions, more accurately thought of as in a solvated condition, provide the dominant species of conductivity. The solvated ion stability decreases with increasing temperature especially since $POCl_3$ has a large molecular volume. Thus it might be expected that a reversal of this equilibrium takes place with the formation of $POCl_3$ at a higher temperature. This behaviour is not restricted to this particular solvent alone, but has been noted for BrF_3 (14) as well as other non-protonic materials.

Information suggesting the above ionic species is given from electrolysis studies of Cady and Taft (13) where Fe^{+3} was reduced to Fe^{+2} in PCl_3. The formation of a highly reactive material at the cathode has been interpreted by the following reactions (1):

$$POCl_2 + e^- \rightarrow (POCl_2)$$

$$2(POCl_2) \rightarrow POCl + POCl_3$$

Clusius and Haimerl (15) have shown that HCl^{35} exchanges chlorine atoms with $POCl_3$ more slowly than with $AsCl_3$ and PCl_3, but more rapidly than with $SiCl_4$ and S_2Cl_2. This implies ionic species. A large number of compounds dissolve in $POCl_3$. The following illustrative list is taken from V. Gutmann (16).

1. Soluble
   - A. Cryosoopicly determined, dissociation occurs: PCl_5, PBr_5, $AuCl_3$, $BiCl_3$, ICl_3, SCl_4, $BiBr_3$, BiI_3, $PtCl_4$.
   - B. Cryosoopic and conductance, monomolecular species: $SiCl_4$, $SiBr_4$, $SnBr_4$, N_2O_5, OsO_4
   - C. Compound formation: $AlCl_3$, BBr_3, $SbCl_5$, $SnCl_4$, $TeCl_4$, $TiCl_4$ BCl_3.
   - D. Tend to associate: $SnCl_4 \cdot POCl_3$, Cl_2O_7.
   - E. Colorless solutions, no knowledge of species: $AsCl_3$, $AsBr_3$, SnI_4, HgI_2, $FeCl_2$, Br_2, $KClO_3$.
   - F. Colored solutions: Cl_2, Br_2, I_2, NaI, $RbICl_2$, $(Ch_3)NI$.
2. Moderate or slightly soluble: KIO_3, $KClO_4$, KIO_4, $FeCl_3$, $Hg(CN)_2$, $HAuCl_4$
3. Electrolytes, dissociates slightly: LiCl, NaCl, KCN, KCNO
4. Insoluble: KNO_3, $K_2C_2O_4$, TlCl, AgCl, HgCl, $CuCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $ZnCl_2$, $CdCl_2$, $CdBr_2$, CdI_2, $MnCl_2$, VCl_3, $K_3Fe(CN)_6$, P_2O_5, CrO_3, I_2O_5.

Most of these compounds have been classified only from a qualitative point of view. Gutmann has established the following numerical data (16):

$POCl_3$ at 20°C.

	Solubility g/l	Specific Cond. at sat. conc.	Equivalent Cond. V=1000 l/Mol
LiCl	0.05	6.6×10^{-6}	4.0
NaCl	0.31	3.0×10^{-5}	6.4
KCl	0.60	3.4×10^{-5}	6.7
NH_4Cl	0.46	3.6×10^{-5}	6.9
RbCl	0.87	8.3×10^{-5}	14.6
CsCl	1.26	1.1×10^{-4}	16.0
$(CH_3)_4NCl$	2.00	5.5×10^{-4}	37.6
KF	0.40	2.6×10^{-5}	6.4
KBr	0.51	4.3×10^{-5}	14.5
KI	1.71	1.2×10^{-4}	23.1
KCN	0.73	3.3×10^{-5}	7.2
KCNO	0.80	3.1×10^{-5}	9.0
KCNS	0.76	2.9×10^{-5}	6.6

Gutmann calls attention to the observations that among the halides of the above list ionization increases, as is evidenced by the conductance values with increasing size of the cation or anion. Such is not the case with KCN, KCNO, and KCNS, which show virtually no change in conductance or solubility. Well definied instances of inorganic compound formation with $POCl_3$ are:

a. $POCl_3 \cdot BCl_3$, rhombic, ΔF_{298} of dissociation equals -4.6 kcal. No BF_3 compound. (17)

b. $SnCl_4 \cdot 2POCl_3$ or $Cl_4Sn(:O:PCl_3)_2$ (18)

c. $2ZrCl_4 \cdot POCl_3$ (19)

d. $3ZrCl_4 \cdot 2POCl_3$ and $3HfCl_4 \cdot 2POCl_3$ (20)

e. $Al_2Cl_6 \cdot 2POCl_3$ (21)

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METHODS FOR PREPARATION OF PURE SILICON

Alex Beresniewicz　　October 28, 1952

Introduction

During World War II high purity silicon was in great demand because of its use as a semiconducting material in crystal rectifiers of radar sets. Impurities, especially non-metallic, have a very marked effect on some physical properties of silicon, mainly on its specific resistance, ρ. (1),(2). Measurements of specific resistance provide, therefore, a very sensitive and accurate method for determining the purity of a given sample. According to Pearson and Bardeen (2) pure silicon should have a resistance of 10^6 ohms cm. at room temperature, but this value has not yet been attained.

Review of the General Methods for Preparation of Silicon

1. Reduction of SiO_2 with C or CaC_2 in the electric furnace.

2. Reduction of SiO_2 with Al in a thermite type reaction.

3. $SiO_2 + 2Mg \rightarrow Si + 2MgO$.

4. Electrolysis of a solution of SiO_2 in a molten mixture of sodium and potassium fluorides. The alkali metal set free by the current reduces SiO_2 to Si.

5. $SiCl_4 + Zn_{vap.} \xrightarrow{900^\circ C.} ZnCl_2 + Si$

6. Reduction of K_2SiF_6 with Zn or Al.

Becket (3) is usually credited with the first successful attempt to prepare pure silicon. He treated the crude electric-furnace product with an HF solution at room temperature, thus extracting most of the Fe impurities. Schaff (4) purified the 99.8% Si by subjecting it to a heat treatment in a nonoxidizing atmosphere. The DuPont Company manufactured pure silicon on a technical scale by reducing $SiCl_4$ with Zn vapor. Their product was found to be free of metallic impurities, as determined spectroscopically (5).

Improved Methods for Preparation of Pure Silicon

Wartenberg tried to prepare silicon of possibly highest purity by the following methods: (6)

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[illegible]

[illegible]

[illegible]

I. Preparation of pure K_2SiF_6
  - A. Reduction with Al
    - Crystallization from molten metals:
      - Al
      - Ag
      - Zn
        - Purification by melting in vacuum
  - B. Electrolysis of fused K_2SiF_6 + NaCl

II. Thermal dissociation of SiI_4

III. Reduction of $SiCl_4$ with Zn vapor

I. Iron-free K_2SiF_6 was prepared by precipitation by addition of KCl to a solution of H_2SiF_6, which was acidified with HCl, and decanting several times with water.

By heating pure K_2SiF_6 with Al and NaCl for two hours at 900°C. a regulus of Si was obtained. Samples of it were melted in quartz crucibles with Al, Ag and Zn respectively. These metals have relatively low melting points and do not form silicides.

Table 1 records the solubilities of Si in Al, Ag and Zn and vice versa.

Table I

Metal	Solubility of Si at 900°C	Solubility of the metal in silicon	
Al	30% by weight	0.15% by wt.	0.14% by vol.
Ag	5%	0.5 - 0.6%	0.15% by vol
Zn	1.6%	0.5 + 0.05% Al	0.16% by vol

Wartenberg next tried to remove the metallic impurities by melting the respective silicon samples in a vacuum oven. After Si_{Ag} had been fused in a sintered corundum boat, its analysis showed the presence of 0.5% Ag and of 0.9% Al. Apparently the Al_2O_3 of the container was reduced by molten silicon. At first this might appear unusual, because the heat of formation of Al_2O_3 is larger than that of 1.5 SiO_2. It can be explained, however, by making use of the approximate form of the Nernst's heat theorem.

Attempts were made to melt silicon in such a manner that it would not be in contact with any wall material. The resulting product was covered with a thin bluish film, probably of Si_3N_4 or SiC.

During electrolysis of molten K_2SiF_6 the cathodically separated alkali metal reduces the melt to silicon. NaCl is usually added in order to depress the dissociation of K_2SiF_6. Silicon prepared by this method is soluble even in 1%HF. Special precautions have to be taken therefore in extracting it from the electrolytic residue. Analysis of the product showed the presence of 0.1% Na, 1%C and of some iron from the graphite crucible.

II. Efforts to prepare pure silicon by thermal decomposition of SiI_4 were unsuccessful. At 1200°C this compound decomposes; silicon crystallizes on a carbon wire, but the iodine recombines only slowly with Si.

III. Zinc vapor reduces $SiCl_4$ but not the SiO_2 of the quartz container.

$$2Zn(vap.) + SiCl_4 \xrightarrow{900^{o}C} Si + 2ZnCl_2; \quad \Delta H = -100 \text{ Cal.}$$

Using this method Wartenberg prepared a product which had a specific resistance of 11000 ohms cm. The product was a fine, wool-like material composed of transparent crystals. (6)

Table 2

Method of Preparation	Impurities % by Vol.	$\rho[\Omega \text{ cm}]$
1. Ideally pure Si	None	10^6
2. $SiCl_4$ + Zn (Wartenberg)	?	1.1×10^4
3. $SiCl_4$ + Zn (Du Pont)	<0.001% C	10^2
4. Sams as (3), only melted before	<0.001% C	50
5. Crystallized from Al or Ag	0.16%	2×10^3 3×10^3
6. Electr. of K_2SiF_6	0.25% Na	10^3

When Si is fused in quartz containers under He atmosphere its specific resistance drops considerably. SiO could be formed, but there is no characteristic absorption band of it (2.73μ) after the melt solidifies. SiO is thermodynamically unstable at 1000°C (7). Wartenberg proposes the following reaction: $2SiO \rightarrow Si + SiO_2$; to take place (6).

The fact that silicon after being melted becomes a much better conductor suggests that it might be contaminated by oxygen. It could come from hot quartz walls (6), and it is known to make silicon an N-conductor. (1)

It seems that the best method for preparation of pure silicon would be to melt a fairly large amount of Si powder in an evacuated quartz container by means of a lens (6). That this is theoretically possible was shown by Stock (8) who melted silicon using a lens 40 cm. in diameter.

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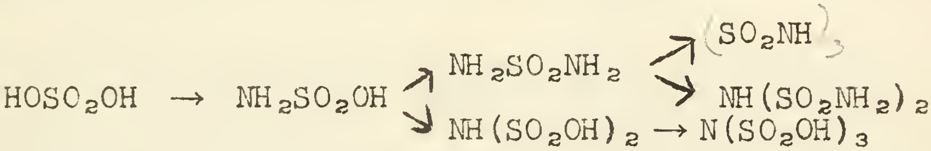
IMIDODISULFINAMIDE

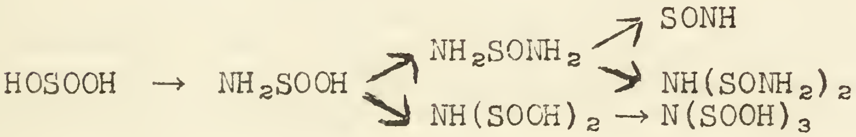
G. R. Johnston November 4, 1952

I. General Introduction

The availability of ammonia has focused attention and aroused interest in the nitrogen system of compounds. This point of view utilizes ammonia as a parent substance and solvent, as compared to the oxygen system of compounds which places water in that role. By the replacement of the oxygen atoms in many oxygen-containing compounds with their nitrogen analogs, many interesting compounds can be visualized. For example, by substituting nitrogen for oxygen in sulfuric and sulfurous acids, a series of related compounds called aquo ammono sulfuric and sulfurous acids can theoretically be postulated:



$$\begin{tikzcd}
 & & & (SO_2NH) \\
 & & NH_2SO_2NH_2 \arrow[ur] \arrow[dr] & \\
HOSO_2OH \arrow[r] & NH_2SO_2OH \arrow[uur] \arrow[dr] & & NH(SO_2NH_2)_2 \\
 & & NH(SO_2OH)_2 \arrow[r] & N(SO_2OH)_3
\end{tikzcd}$$



$$\begin{tikzcd}
 & & & SONH \\
 & & NH_2SONH_2 \arrow[ur] \arrow[dr] & \\
HOSOOH \arrow[r] & NH_2SOOH \arrow[ur] \arrow[dr] & & NH(SONH_2)_2 \\
 & & NH(SOOH)_2 \arrow[r] & N(SOOH)_3
\end{tikzcd}$$

Of the two similar series of compounds, more is known concerning the aquo-ammono sulfuric acids than is known about the aquo-ammono sulfurous acids. Most of the imides and amides of sulfuric acid have been recognized as stable substances and can be obtained readily by reacting either sulfur trioxide or sulfuryl chloride with ammonia. On the other hand, less is known about the reactions of either sulfur dioxide or thionyl chloride to give the corresponding imides and amides of sulfurous acid.

II. Historical Developments

There is some confusion in the earlier literature regarding the products of reaction between sulfur dioxide and ammonia.

In 1826, Dobereiner (1) described the product as a brownish-yellow vapor which quickly condenses to a bright brown solid mass which he called anhydrous ammonium sulfite, which is converted into the hydrate with a trace of water.

In a series of three papers, Rose (2,3,4) concluded that the same product is obtained regardless of the ratio of sulfur dioxide to ammonia. Rose found that the compound obtained contained equimolar quantities of sulfur dioxide and ammonia and was either orange-red and viscous or a red crystalline material. He named this material ammonium sulfite or anhydrous ammonium bisulfite.

It was not until almost sixty years after the work of Rose that Schumann (5) undertook his investigations of this reaction. Schumann assumed that the products reported earlier were decomposition products and not, in themselves, direct products of the reaction. Working at temperatures around 0°C., he succeeded in isolating two products. The first, $SO_2 \cdot NH_3$, was obtained using an excess of sulfur dioxide; and the second, $SO_2 \cdot 2NH_3$, using an excess of ammonia. The former compound is a yellow powder which he found to be amidosulfinic acid, NH_2SOOH, while the latter is a hard, red material which he termed the ammonium salt of amidosulfinic acid. The amidosulfinic acid is very hygroscopic and is also decomposed by moisture. into a white powder of variable composition. Ammonium amidosulfinate was also obtained as a very viscous material.

In the same year, Divers and Ogawa (6) found that sulfur dioxide reacts with excess ammonia in an ethereal solution at low temperatures to give, not a red material as the product Schumann had obtained, but, instead a white powder. This compound was also found to have the molecular composition $SO_2 \cdot 2NH_3$. It was found to be very deliquescent; on exposure to air, it decomposed, evolving ammonia to form an orange colored substance. Divers and Ogawa concluded that ammonium amidosulfinate is the first product of the reaction, which subsequently underwent decomposition to give diammonium imidosulfinate (6,7,8) and ammonia.

$$SO_2 + NH_3 \rightarrow NH_2SOONH_4 \rightarrow NH(SOONH_4)_2 + NH_3$$

Ephraim and Piotrowski (9), a few years later, confirmed Schumann's results as to the product obtained from excess sulfur dioxide and ammonia, but disagreed with Divers and Ogawa over diammonium imidosulfinate as the final product of the reaction between sulfur dioxide and excess ammonia at room temperatures. They isolated a red material of molecular composition $2SO_2 \cdot 4NH_3$ which they called triammonium imidosulfinate, $NH_4N(SOONH_4)_2$. They succeeded, also, in preparing the trisilver salt, $AgN(SOOAg)_2$. These workers also studied the reaction between thionyl chloride and ammonia, assuming that imidodisulfinamide, $NH(SONH_2)_2$, should be obtained. Thionyl chloride reacts with excess liquid ammonia to give an intensely red-colored solution; and the stable, red residue, after the evaporation of the solution, was added to an ammoniacal silver nitrate solution to give the same trisilver salt as obtained from triammonium imidosulfinate. Ephraim and Piotrowski assumed that the imidodisulfinamide formed initially is hydrolyzed to diammonium imidosulfinate:

$$NH(SONH_2)_2 + 2H_2O \rightarrow NH(SOONH_4)_2.$$

They also assumed that the red color of the liquid ammonia solution is due to the conversion of imidodisulfinamide into an ammonium salt, $NH_4N(SONH_2)_2$,

Divers and Ogawa discovered two other compounds as products of the decomposition of ammonium amidosulfinate. The first was a compound $4NH_3 \cdot 5SO_2$ or $N_4H_{12}S_5O_{10}$ (7). They could not assign a structure to it, but Ephraim and Piotrowski (9) assumed it to be a chain-like molecule:

$$HOSO\text{-}NHSO\text{-}NHSO\text{-}NHSO\text{-}NHSOOH \cdot 3H_2O.$$

The second compound (8) was assumed to be sulfamide.

Since substituted sulfinimides can be prepared (10) by reacting amines with thionyl chloride:

$$SOCl_2 + RNH_2 \rightarrow SONR + 2HCl,$$

Schenk (11) in 1942 attempted and was successful in the preparation of sulfinimide:

$$SOCl_2 + NH_3 \rightarrow SONH + 2HCl.$$

This substance was found to be unstable, however, and polymerized at -60°C. to a chain polymer. Schenk regarded the imidodisulfinamide, which Ephraim and Piotrowski thought they had obtained, as an ammonolysis product of sulfinimide.

Jander, Knoll, and Immig (12), utilized the reaction between liquid sulfur dioxide and ammonia to obtain the same yellow compound $SO_2 \cdot NH_3$ previously obtained by the gas-phase reaction; but they assumed it to be thionyl ammonium sulfite, $[(NH_3)_2SO]SO_3$.

Recently, Goehring and Kaloumenos (13) have examined the properties of $SO_2 \cdot NH_3$. The compound prepared at low temperature gave a quantitative yield of ammonium and bisulfite ion, while the compounds formed at higher temperature gave in addition trithionate ion, sulfate ion, and thiosulfate ion. Decomposition of $SO_2 \cdot NH_3$ occurs at 80°C., yielding amidosulfonate, imidodisulfonate N_4S_4, sulfur, and N_2S_4.

III. Imidodisulfinamide

In spite of the results of Ephraim and Piotrowski; Goering, Kaloumenos, and Messner (14) attempted the preparation of imidodisulfinamide. They were successful in preparing this compound in two ways: first by reacting ammonia with sulfur dioxide, and second, by reacting ammonia with thionyl chloride, the ammonia used in excess in each instance.

The first reaction was carried out by bringing together the dry gases at a temperature of -15 to -20°C. The orange-red $SO_2 \cdot 2NH_3$ melts at 0°C. to a dark violet liquid; the melt was extracted with nitrobenzene. The nitrobenzene extract was heated to 80-100°C. until all of the ammonia had been driven off and subsequen

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cooling produced yellow crystals of imidodisulfinamide. From 40 g. of $SO_2 \cdot 2NH_3$, 0.3-0.75 g. of $NH(SONH_2)_2$ were obtained.

Desiring to improve the yield, the second reaction was carried out by dropping thionyl chloride onto liquid ammonia at -80°. After evaporation of the ammonia,,a yellowish red substance was obtained; this product when subjected to the same treatment as above, yielded imidodisulfinamide. From 25 g. of $SOCl_2$, 10-15 g. of $NH(SONH_2)_2$ was obtained.

Imidodisulfinamide and its aqueous solution are stable. The aqueous solution is surprisingly stable towards oxidation. It is reduced by potassium iodide in 100% formic acid to give sulfur and sulfate ion. A trisilver salt, $AgN(SONHAg)_2$, was prepared from the amide. This salt possesses light yellow color and is stable for several hours.

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LIESEGANG RINGS

Richard F. Heitmiller November 11, 1952

Introduction:[1,2]

When a drop of concentrated silver nitrate solution is placed on a film of gelatin containing potassium dichromate, the silver chromate is not precipitated continuously but in the form of a number of concentric rings; rhythmatic precipitates of this kind are called Liesegang rings. These banded structures have been observed to be of two types: those in which the rings are separated by clear spaces, and those in which the precipitate is separated by a band of peptized sol, i.e. alternate bands of different colors occur in an otherwise continuous deposit.

Factors Effecting Formation:[3,4,5,6,7,8,9,10,11,12,13,14,15]

Much work has been done on this subject, and the ring formation has been observed with many precipitates and with gels of different materials. However, the nature of the gel is not of fundamental importance since banded structures have been obtained by precipitation of many salts in aqueous solution in the absence of any gel-forming substance, provided there is a restriction to movement by convection etc., as in a capillary tube. We can state, therefore, that although the presence of the gel is not essential, its presence appears to facilitate rhythmic instead of continuous precipitation, and its influence is to some extent specific. It has been found, for example, that beautiful rings of selenium metal are produced in gelatin when selenous acid is reduced either by ferrous sulfate or stannous chloride, but this tendency to form fine banded structures decreases when agar-agar is used, and no bands at all occur in a starch gel.[16] The nature of the Liesegang rings can be altered in the same manner. Silver tungstate gives sharp banded structures of type I in agar-agar, while in starch-gel, structures of the type II are obtained.[15,16]

Light also plays an important role in the formation of Liesegang rings: in general more rings are formed if the rings are allowed to develop in the light, than if they are allowed to develop in the dark. In the case of gold Liesegang rings, the formation will only take place in the presence of light. However, under conditions where silver tungstate forms sharp bands of type I in the light, under similar conditions, but in the dark, the number as well as the thickness of the bands are increased and the rings obtained are of a spiral nature.[16]

Explanation: The Diffusion Theory

From a survey of the literature it has been observed that, all other conditions remaining constant, (concentration of gel and dissolved electrolyte, temperature, light, etc.) the number of rings decrease with a decrease in concentration of the diffusing electrolyte, and that the distance between two consecutive rings usually increases as the diffusion proceeds downward. A mathematical expression has been derived for treating the ring formation as a diffusion phenomenon.[17] For the precipitation of silver chromate it has been postulated, that as silver ions diffuse into the chromate contained in the gel, reaction occurs, but the silver chromate remains for a measurable time in the colloidal state and a visible precipitate does not form. The depletion of the chromate ion concentration causes chromate ions to diffuse rapidly into the reaction zone. Precipitation of the silver chromate might then be induced by the accumulation of the ions of potassium nitrate, and at this point some potassium chromate could be absorbed causing a further depletion of chromate ion. Since the rate of diffusion is most rapid where the concentration gradient is greatest there will be a region in the vicinity of the precipitation zone where the concentration is low. It will then be necessary for silver ions to diffuse some distance into the gel before reaching a zone in which chromate ion concentration is sufficient for colloidal silver chromate to be formed, at which point the cycle is repeated until all of the silver chromate ion is exhausted.

In a recent paper on this subject it has been stated that nickel and zinc cyanide; nickel, zinc and cobalt ferrocyanide; barium and mercurous vanadate; cerous oxalate and carbonate rings in gelatine, and thorium hydroxide, thallium oxide, and uranium carbonate in agar-agar belie the diffusion theory since in each case the distance between consecutive precipitation zones becomes less and less with the dilution of the diffusing electrolyte. The author does not present an alternate explanation.[16]

Banded effects are frequently found in nature, and it is possible that rhythmatic precipitation may be important in this connection. Liesegang developed the view that the banded agates were formed in a manner analogous to rhythmatic precipitation in gelatin, but his theory is not universally accepted. It is important to remember that periodic structures are not all necessarily due to the same cause.

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FORCE CONSTANTS IN POLYATOMIC MOLECULES

Donn D. Darsow November 4, 1952

I. Definition and Calculation of Force Constants

A stretching force constant is a molecular constant associated with the chemical bond between two atoms. Numerically it is the force in dynes that would be acting to restore a bond distance if the two atoms were somehow momentarily displaced one cm from their equilibrium distance in the ever-vibrating molecule, assuming that the same proportionality of restoring force to amount of bond displacement prevailed at such fictitious gigantic distortions (4) p. 84.

Stretching force constants (also called bond or valence force constants (4) or valence force potential constants (10)) have magnitudes in range of 0.01×10^5 to 25×10^5 dynes/cm (4). Bending force constants (4) are associated with the forces tending to restore distortions of angles between three bonded atoms. They have different ranges of magnitudes from and are negligible compared to stretching force constants in linear triatomic molecules.

For illustrative purposes I will consider only linear triatomic molecules A-B-C (eg. HCN, ClCN, BrCN, ICN, N_2O, CO_2, CS_2, OCS) (1), (10). In such molecules the atoms are continually vibrating along their common axis. The two pairs of atoms A-B and B-C each have a fundamental frequency of vibration which is dependent on their atomic masses and the forces between the two atoms. Each vibrating motion approximates simple harmonic motion (departing somewhat for the very small amplitudes), has a fundamental frequency, and gives characteristic fundamental and overtone bands in the infra red spectrum of the molecule (7).

The stretching force constant of the bond is defined by the following equation (7), (11) pp. 148, 501:

$$(1) \qquad \omega = \frac{1}{2\pi}\left[\frac{f_{ab}}{\frac{1}{m_a}+\frac{1}{m_b}}\right]^{\frac{1}{2}}$$

ω = fundamental vibrational frequency

f_{ab} = stretching force constant in dynes/cm

m_a, m_b: masses of the 2 atoms, in atomic mass units.

Certain corrections for anharmonicity of the vibrations, if known, can be applied when greatest accuracy is desired.

Force constants are calculated the most precisely from the vibrational frequencies determined spectroscopically. Such determinations of frequencies are not always possible however. An alternative method is to calculate the force constant value from the interatomic distance (the bond length) using empirical relations, such as Gordy's.

There has long been observed a definite regularity in the variation of force constants and bond lengths in all series of similar molecules that have been so studied, (7) pp. 453ff. One notes that in all cases the force constant increases as bond length decreases, (1)(2)(3)(7)(10). As yet no theoretical derivation between force constants and bond length has been advanced. But several empirical relations between force constants and bond

lengths have been developed (2)(7) by comparing force constants and bond lengths for many known molecules.

In 1946 Gordy (2) presented such a relation which has been quite successful in many cases. This rule is formulated as follows:

$$(2) \qquad f_{ab} = c \cdot N_{ab} \left[\frac{X_a \cdot X_b}{R_{ab}} \right]^{\frac{3}{4}} + d$$

f_{ab} = stretching force constant for bond A-B in units of 10^5 dynes/cm

N_{ab} = bond order

R_{ab} = equilibrium bond length in Å

X_a, X_b: electronegativities of atoms A and B

c,d: constants whose value depends on the rows in the periodic table of the atoms A and B. Table given by Gordy (2).

This equation gives force constant values within an average of two percent of the spectroscopically determined force constants for all molecules to which it has been applied (2).

The concept of bond order, N, is intimately related with bond lengths, with force constants and with the nature of chemical bonds. The bond order is a relative measure of the electron density between bonded atoms (2)(12)(13). Otherwise stated, it is the effective number of single (those involving only two electrons) bonds existing between two atoms. This applies to both extreme ionic and extreme covalent bonds and also to those intermediate, where the partial ionic and partial covalent character (Pauling (6), pp. 171ff) are considered additive (2). Bonds in molecules whose atoms have their usual valencies satisfied have essentially pure bond types. Typical pure single, double, and triple bonds are those in HCl, CS_2, and N_2. These bonds have bond orders of 1.00, 2.00, and 3.00, respectively. (See extensive table of bond orders of Gordy (2)).

An empirical relation between bond order, N, and bond length, R, has been developed by Gordy (3)

$$(3) \qquad N_{ab} = \frac{c'}{R_{ab}^{2}} + d'$$

N_{ab} = bond order for A-B

R_{ab} = bond length of A-B in Å

c';d': constants that have particular values for particular pairs of bonded atoms. Table given by Gordy (3).

This equation yields bond orders from the otherwise determined bond lengths. Equation (3) is frequently used to calculate the bond order value to be inserted into equation (2) when using the latter to calculate force constants.

II. Significance of Force Constants

Force constants are admittedly a theoretical concept of pure chemistry

which are mainly useful to the investigator who is interested in the forces between atoms and the nature of chemical bonding. Force constant values must be based ultimately on other fundamental quantities, such as bond lengths or vibrational frequencies. They do not give us any additional facts. They do present this experimental knowledge in new forms that give increased internal consistency to the current meager but growing understanding of the chemical bond.

Perhaps the most important use of force constants is aiding in the examination of spectra. Force constants that have been reliably determined for a particular bond can sometimes be utilized to calculate or identify the vibration frequencies of that bond.

III. Estimation of Force Constants of Triatomic Molecules by a Comparison Method

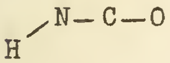
There are instances where errors substantially larger than 2 o/o result from calculating a force constant value only from the bond length, electronegativities, and Gordy's equations (2) and (3) (see reference (2), Table I). It is desirable to have a more accurate method for use when vibrational frequency data are not known for a molecule. The two recent papers of Thomas, (1)(10), present the following method which purports to do this.

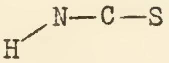
By solving certain secular equations involving the force constants of a molecule, the force constants may be expressed in terms of a parameter, p, which may have a large range of possible values (9)(10). Thus a large number of possible sets of the force constants for the molecule are obtained. These are most conveniently represented by graphing the p vs. f values. If the one correct p value could be obtained, the correct value of all the force constants would be indicated. Thomas obtains this correct p value by calculating the force constant of one of the bonds in the molecule from the knowledge of the ratio of bond lengths of that bond and the length of the same bond in a similar "reference molecule", the force constant of which bond is accurately known. The ratio of the bond orders is then calculated and used with the ratio of bond lengths in Gordy's equation (2) to calculate the force constant of the bond in the molecule being investigated. The significant feature of this method is that a comparison with the reference molecule force constant value is employed.

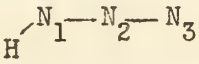
In (10) Thomas applies this method to calculate force constant values for ClCN, BrCN, ICN and OCS. HCN was the reference molecule used for the cyanogen halides and CS_2 was used for OCS. Vibration frequencies which have been since determined for OCS have given the precise value of the force constant for OCS. Thomas' value checks within two percent with it.

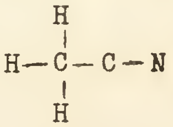
IV. Extension to Other Polyatomic Molecules

Thomas (1) then makes an interesting extension of his method to the non-triatomic molecules









which have the angular shapes indicated, the three heavy atoms being collinear in each case. He states that "the motions of the H atoms are not coupled to any great extent with those of the rest of the molecule and to a good approximation the CH_3 and H—N groups may be considered as rigid groups."

He makes the interesting but otherwise unsubstantiated implication that the vibrational (and force constant) characteristics of these molecules should be very similar to their isoelectronic counterparts, respectively, O−C−O, O−C−S, and O−N_2−N_3. Accordingly he uses these as the reference molecules for calculating values for their force constants, using the f-p comparison method as in (10). He uses HCN as the reference molecule for CH_3CN. Strangely, Thomas (1) tabulates vibration frequencies for each of these molecules but does not mention whether the force constant values have been calculated from these, or, if so, whether they are in agreement with the values resulting from his method.

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METATHESIS IN LIQUID ARSENIC TRICHLORIDE[1]

Harold J. Matsuguma November 11, 1952

Introduction:

About fifty years ago Walden (2) recognized liquid arsenic trichloride as an ionizing, non-aqueous solvent. He found that binary salts and quarternary ammonium salts are soluble in this solvent. The recent finding that water-free arsenic trifluoride is a solvent in which metathesis is possible has revived interest in Walden's observations.

Properties of Liquid Arsenic Trichloride:

Arsenic trichloride has many of the desirable properties of an ionizing, non-aqueous solvent. Physical properties of the pure solvent are summarized in Table 1. According to Raman spectra the molecules of this compound possess a pyramidal structure.

Table 1

Molecular Weight	181.28 g/g-mole
Melting Pt.	-18°C.
Boiling Pt.	130.2°C. (2,3)
Specific Conductivity (0°)	1.4-1.6 x 10^{-7} Ω^{-1}x cm^{-1}
Density of liquid at melting pt.	2.163
Dielectric constant	12.8 (20°) (4,5)
	12.35 (21°) (4,5)
Specific refractivity	0.2732
Molar volume at the melting pt.	83.8
Ebullioscopic constant	6.48-7.25 (6)
Heat of formation of the liquid	71.4 Kcal/g (7)
Parachor	212.0 (8)
Heat of vaporization	69.7 cal/mole
Critical temperature	356°C.
Paramagnetic susceptibility	7.39 x 10^{-6}
Dipole moment in benzene	2.15 (9)
Dipole moment in dioxane	3.11 (9)
Decomposition voltage in nitrobenzene	0.78 v (10,11,12)

General:

According to Walden (2), and confirmed by Gutmann (1), the self-ionization of arsenic trichloride may be expressed by the equation: $2AsCl_3 \rightleftharpoons AsCl_2^+ + AsCl_4^-$. Therefore, substances capable of forming $AsCl_2^+$ or $AsCl_4^-$ ions in arsenic

trichloride would represent acids or bases, respectively. It was hoped that neutralization reactions between such compounds in liquid arsenic trichloride would lead to the formation of hitherto unknown types of complex chlorides.

Arsenic trichloride dissolves many different substances whose solutions are much better conductors than the pure solvent itself. The solubility relationships of various compounds and elements in arsenic trichloride are summarized in Table II. Reactions between the solvent and several compounds dissolved in it are given in Table III. Some reactions between arsenic trichloride and organic compounds are summarized in Table IV. Figure 1 depicts the considerable increase in the conductivity of a solution of tetramethylammonium chloride in arsenic trichloride as a function of concentration.

Table II

Solubility Relationships in Arsenic Trichloride

Soluble	Less Soluble	Slightly soluble	Insoluble
$(CH_3)_4NAsCl_4$	$[(CH_3)_4N]SnCl_6$	K_2CO_3	$KMnO_4$
$(CH_3)_4NSnCl_5$	$(CH_3)_4NTiCl_5$	K_2SO_4	Cr_2O_3
$(CH_3)_4NVCl_5$	$Fe_3Fe(CN)_6$	KNO_3	Nb_2O_5
$(CH_3)_4NSbCl_6$	LiCl	AgCl	Ta_2O_5
KI	NaCl	$MgCl_2$	MoO_3
HCl	NH_4Cl	$BaCl_2$	WO_3
RbI	KCl	$BaBr_2$	TiO_2
ICl	RbCl	VCl_3	CuO
Cl_2	CsCl	V_2O_5	Cu
Br_2	$NbCl_5$	$CrCl_3$	Ag
I_2	$TaCl_5$	Fe_2O_3	Au
S	P_2O_5	$FeSO_4$	Mg
P	KCN	MnO_2	Si
$AlCl_3$		CuCl	Ti
$TiCl_4$		$CuCl_2$	Nb
$SnCl_4$			Ta
$(CN)_2$			Cr
$COCl_2$			Mo
NOCl			Pt
PCl_5			Fe
$SbCl_3$			V
$SbCl_5$			W
$FeCl_3$			
HgI_2			
CoI_2			
AsI_3			

Table III

Some Reactions in Arsenic Trichloride

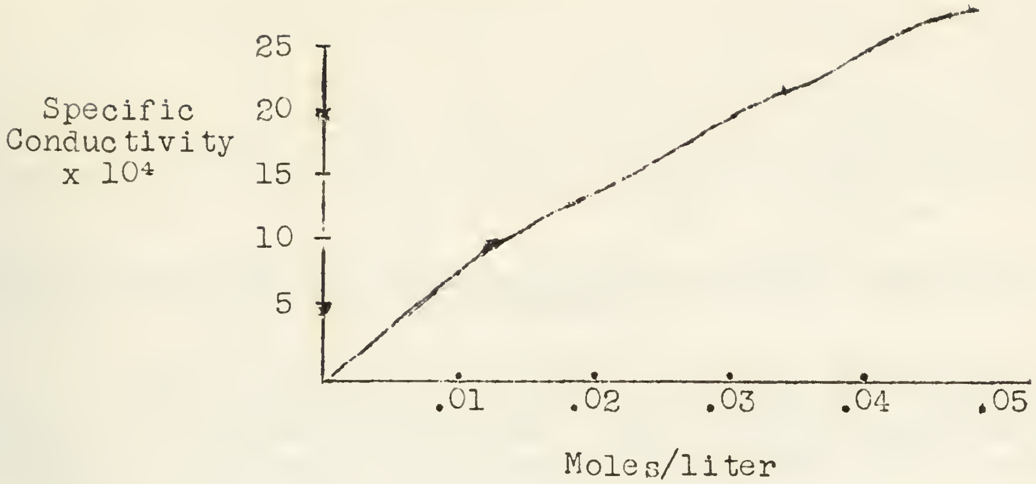
Starting Product	Reaction Product	Observations
$(CH_3)_4NCl$	$(CH_3)_4NAsCl_4$	
C_2H_5I	AsI_3	(13)
HgO	$HgCl_2$	With heating
BBr_3	BCl_3 and $AsBr_3$	(14)
NH_3 (liq.)	$AsCl_3 \cdot 4NH_3$	(15)
N_2O_4	As_2O_5, HCl and NOCl	
PH_3	AsP_3 and HCl	(16)
PI_3	PCl_3 and AsI_3	(17)
PbO_2	$PbCl_2$	With heating and shaking
AsH_3	Arsenic and HCl	
H_2S	As_2S_3 and HCl	(18)
Cr_2O_3	Heterogenous powder	
KIO_3	Not investigated	
HI	AsI_3 and HCl	
SnI_4	AsI_3 and $SnCl_4$	(19)

Table IV

Reactions of Organic Compounds

Starting Product	Reaction Product
$(C_2H_5)NH_3Cl$	$[(C_2H_5)NH_3]_2AsCl_5$ (20)
$(C_2H_5)_2NH_2Cl$	$(C_2H_5)_2NH_2AsCl_4$ "
$(CH_3)NH_3Cl$	$(CH_3NH_3)_3As_2Cl_9$ "
$(CH_3)_2NH_2Cl$	$(CH_3)_2NH_2AsCl_4$ "
$(CH_3)_3NHCl$	$[(CH_3)_3NH]_2As_3Cl_{11}$ "
Guanidine	$[H_2NC(NH)NH_3]_3As_2Cl_9$ "
Pyridine	$C_6H_5NHAsCl_4$ "
Quinoline	$(C_9H_7NH)_2As_3Cl_{11}$ "
Quinoline	$C_9H_7NHCl \cdot AsCl_3 \cdot 2H_2O$ (21)

Figure 1



Specific conductivity of solutions of $(CH_3)_4NAsCl_4$ in liquid arsenic trichloride at 20° C.

Gutmann prepared arsenic trichloride by the direct chlorination of the metal. The initial product was yellow due to the presence of excess chlorine. Excess chlorine was removed by bubbling a stream of dry nitrogen through the liquid and by repeated distillations under reduced pressure. The final product was obtained as a colorless liquid whose specific conductivity varied between 3 and 6×10^{-7} $\Omega^{-1} \times cm^{-1}$.

Isolation of Bases from Liquid Arsenic Trichloride:

Compounds of the type $Me^{I}AsCl_4$ were considered bases in liquid arsenic trichloride, but very few such compounds have been reported up to this time. The dimethylammonium and pyridine salts are known and two salts, $Rb_3As_2Cl_6$ and $Cs_3As_2Cl_9$, had been prepared by Wheeler (22). The alkali metal chlorides were found to be only slightly soluble in liquid arsenic trichloride. However, the residue upon evaporation of a solution of potassium chloride in arsenic trichloride was found to correspond to the formula $KAsCl_4$ upon analysis. When this compound was prepared in an ignition tube at 250° there was no increase in the yield, showing that only the portion of the chloride which did dissolve would form the compound.

A solution of tetramethylammonium chloride in arsenic trichloride was evaporated under reduced pressure until all of the solvent had distilled off. The residue was a pure white, nonhygroscopic powder which was stable to temperatures up to 175° and which had the formula $(CH_3)_4NAsCl_4$. For neutralization reactions tetramethylammonium chloride was added to solutions of solvo-acids in arsenic trichloride rather than adding the base itself. The end result was the same in both cases.

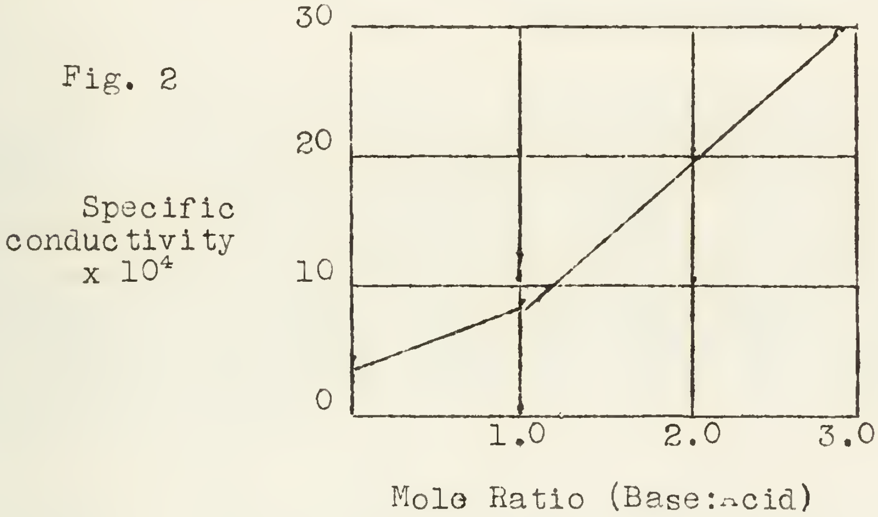
Isolation of Acids in Liquid Arsenic Trichloride:

The compounds $TiCl_4$ and $SnCl_4$ were found to be very soluble in liquid arsenic trichloride and to exhibit acid character in solution. VCl_4 was found to be much less soluble, but nevertheless, a weak acid in the arsenic trichloride. $SbCl_5$ was found to dissolve in arsenic trichloride and a compound corresponding to the formula $AsSbCl_8$ was isolated from the residue of such a solution. Since that solution exhibited acid characteristics, the compound was assigned the formula $AsCl_2SbCl_6$.

Metathesis and the Formation of Pentachloro Complexes of Tetravalent Titanium, Tin and Vanadium:

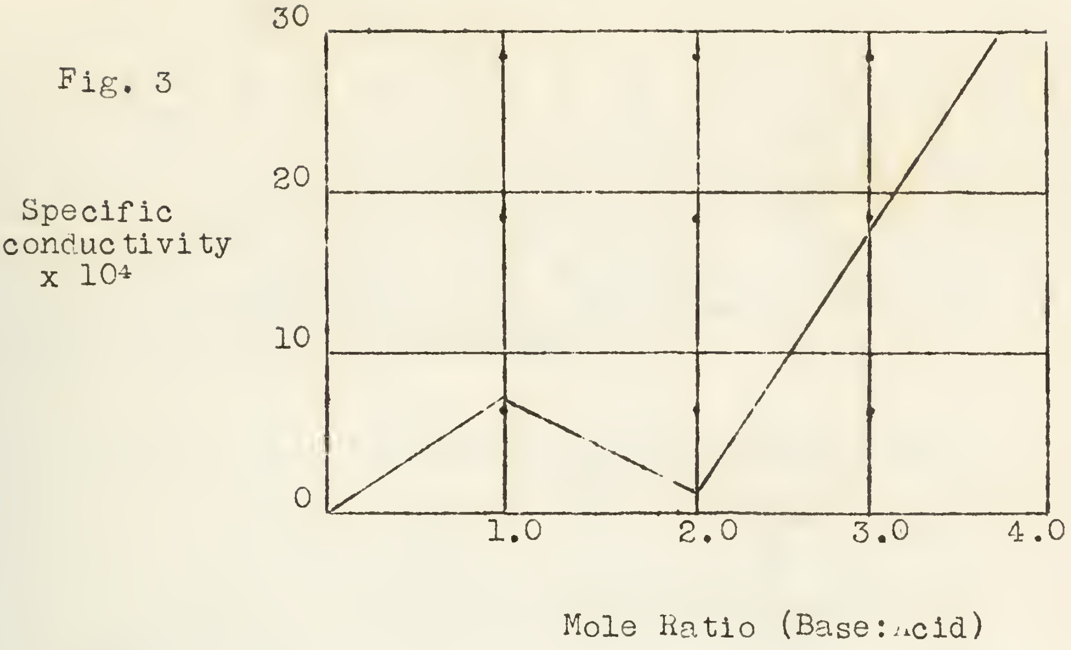
Figure 2 depicts the course of the conductimetric titration when tetramethylammonium chloride is added to a solution of $SbCl_5$ in arsenic trichloride. When the mole ratio of 1:1 was reached there was a sharp break in the curve and a subsequent steady, marked rise in the conductivity.

Fig. 2



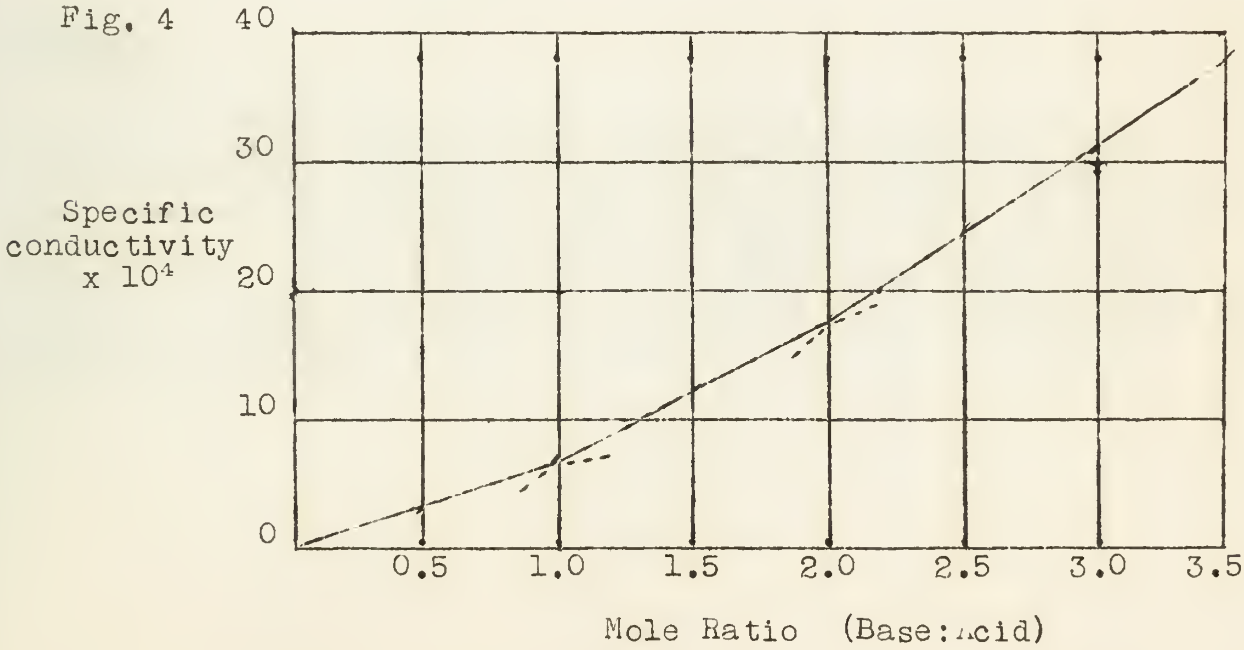
In the case of the neutralization of a solution of $SnCl_4$ in arsenic trichloride the reaction was found to proceed in two distinct steps. (See Figure 3) The maximum point (1:1) represented the formation of the pentachlorostannate(IV) salt. The addition of more base caused the formation of the less soluble hexachloro complex and the subsequent decrease in the conductivity. Once the latter complex had been completely formed, conductivity again increased steadily due to the presence in the solution of the excess base ions. Gutmann actually isolated the two compounds tetramethylammonium pentachlorostannate(IV) and bis(tetramethylammonium) hexachlorostannate(IV) by evaporating solutions of $SnCl_4$ and tetramethylammonium chloride in arsenic trichloride. These compounds are light yellow, hygrscopic solids.

Fig. 3



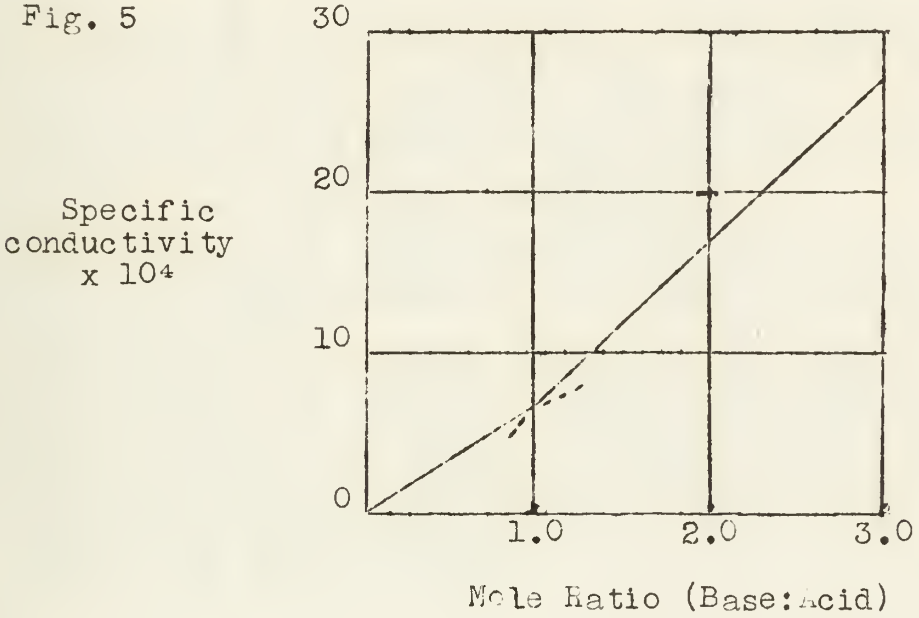
The behavior of $TiCl_4$ toward neutralization with tetramethylammonium chloride in a solution of arsenic trichloride was found to be exactly analogous to that of $SnCl_4$. The curve shown in figure 4 shows two distinct breaks. The first is caused by the formation of the soluble pentachlorotitanate(IV) complex and the second, by the formation of the more soluble hexachlorotitanate(IV) complex. The final sharp increase was caused by the addition of excess base. In this case too gutmann was able to isolate both chloro complexes. Both are light yellow, hygroscopic solids.

Fig. 4



With the addition of tetramethylammonium chloride to a solution of VCl_4 there was found only one break in the conductivity titration curve (Figure 5). The increase in conductivity was caused by the formation of the soluble pentachlorovanadate (IV) compound. The absence of any other break in the curve showed that no hexachlorovanadate(IV) compound was formed. The compound tetramethylammonium pentachlorovanadate(IV) prepared by Gutmann was a dark reddish-violet powder, readily soluble in water to give a bluish-green solution. This compound could not be obtained completely free of arsenic. Since VCl_4 is a weak acid in arsenic trichloride, the presence of arsenic in the product was due to solvolysis.

Fig. 5



Summary:

Water-free arsenic trichloride is an ionizing, non-aqueous solvent in which metathetical reactions are possible. Such reactions produce complex chlorides of the elements titanium, tin, antimony and vanadium. The compound potassium tetrachloroarsenite(III) was also prepared by reaction in liquid arsenic trichloride. $TiCl_4$, $SnCl_4$, VCl_4 and $SbCl_5$ were found to be acids in arsenic trichloride. A solution of tetramethylammonium chloride in liquid arsenic trichloride provided a strongly basic solution.

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THE RHENIDE OXIDATION STATE

Robert L. Rebertus November 18, 1952

I. Chemical Studies

In 1937, Lundell and Knowles (1) found that if a cold solution containing potassium perrhenate and sulfuric acid is passed through a Jones reductor, the rhenium(VII) is reduced to rhenium(-I). Eight equivalents of oxidizing agent were required to oxidize one equivalent of the rhenide to perrhenate. These investigators point out that rhenium has lower oxidation states analogous to the halogens, and they speculated that if a solution containing rhenium(-I) and sulfuric acid is warmed, hyporhenous acid (HReO) and sulfur dioxide should be produced.

The reducing effects of lead, cadmium, bismuth, and zinc amalgams on potassium perrhenate in sulfuric acid and hydrochloric acid media were studied by O. and F. Tomicek (2). Bismuth amalgam in 80% sulfuric acid yielded blue solutions in which Re(VII) was reduced by 2.2 valency units. In 40-50% sulfuric acid solution, brown solutions of Re(IV) were obtained. Lead amalgams in 10% hydrochloric acid and cadmium amalgams in 20-25% sulfuric acid gave a solution containing Re(IV). Only saturated zinc amalgam in 10% hydrochloric acid reduced the Re(VII) to Re(-I).

Lingane (3) has confirmed the reports of Lundell and Knowles (1) and of Tomicek (2). He prepared rhenide solutions by reducing potassium perrhenate in a Jones reductor. The reduced solutions were run directly from the reductor into an excess of standard ceric sulfate solution under an atmosphere of nitrogen, and the excess ceric ion was back titrated with a standard ferrous ammonium sulfate solution, using Ferroin as an indicator. Table I shows the results obtained.

TABLE I

Oxidation State of Reduced Rhenium Solutions

$KReO_4$ Millimolar	Volume reduced solution, cc.	0.01 N $Ce(SO_4)_2$, cc.	Equiv. Ce(IV) per mol total Re
0.105	37.6	3.26	8.3
.209	33.3	5.28	7.6
.418	36.4	12.1	8.0
.836	35.2	23.0	7.8

The analogy between rhenide and halide ions suggested by Lundell and Knowles (1) was extended by Rulfs and Elving (4), who reasoned that thallous rhenide, like the thallous halides, should be relatively insoluble. A rhenide solution of known concentration was prepared. This solution was saturated with thallous chloride at 25° and then was allowed to stand under nitrogen for ninety minutes at 0°. White crystals, isomorphous with thallous chloride, separated from the solution. Although the crystals were not analyzed, they were presumed to be thallous rhenide. The solubility of the thallous rhenide estimated from the known rhenide concentration in the presence of excess thallous ion was approximated to be at least 39 mg. per 100 ml. of 2.4 *N* hydrochloric acid at 0°. The solubilities of the thallous halides in mg. per 100 ml. water at 0° are: TlCl, 161; TlBr, 22; TlI, 2.

Maun and Davidson (5) attempted to prepare more concentrated solutions of Re(-I) than those prepared by Lundell and Knowles (1) (10^{-4} *F*) and Lingane (3) (8×10^{-4} *F*) by reducing hydrochloric acid solutions of perrhenate in a Jones reductor. They were unable to reduce quantitatively Re(VII) to Re(-I) if the initial Re(VII) concentration was greater than 0.001 *F*. Table II shows the results of some of their experiments.

TABLE II

Apparent Average Oxidation Numbers of Reduced Rhenium Solutions

$HReO_4$ *F*	HCl *F*	Time of Reduction minutes	Average Oxidation No. with $Ce(SO_4)_2$	with KIO_3	with I_2
0.00097	4	3-5	0.1		
0.00097	4	3-5	-1.4		
0.00097	4	3-6	-0.9		
0.00242	6	2-3	-0.3		
0.00242	6	2-3	0.5		
0.00483	4	3-5	2.4		
0.00483	4	3-5	-0.2, 0.1	-0.4,0.4	0.6,0.8
0.00504	4	3-5	0.6, 0.7	0.8, 1.0	0.7,0.8
0.00970	4	3-5	2.9		

The average oxidation numbers listed were claculated on the basis of the initial formality of the perrhenic acid. It is believed that the incomplete reductions resulted from the precipitation of rhenium in the reductor. The resulting solutions would contain pure Re(-I) but at a lower concentration than the initial Re(VII) concentration. The solutions obtained from the reductor were colorless which fact supports the explanation of the incomplete reductions.

The possibility of concentrating Re(-I) by volatilization or by evaporating the solutions was also studied by Maun and Davidson (5). No volatility of Re(-I) resulted, and a brown solid residue, which resulted from volatilizing the hydrochloric acid and water from the rhenide solution, was shown by analysis with Ce(IV) to contain rhenium in an intermediate oxidation state.

Highly colored intermediate oxidation states were formed when rhenide was treated with perrhenate, copper sulfate, or oxygen (5). From spectrophotometric studies of the reactions of Re(-I) with perrhenate and oxygen, and from analyses on the reaction product of Re(-I) with copper sulfate or oxygen, the first oxidation product was concluded to Re(I), which is followed by the formation of Re(IV). It is to be noted that the compound Re_2O has been prepared (6) and that a solution possibly containing Re(I) from the reduction of Re_2Cl_6 has been described (7).

Recently, Kleinberg (8) and his coworkers succeeded in isolating a potassium rhenide-potassium hydroxide mixture. Potassium perrhenate (0.003 M) in ethylenediamine-water solution (9.8 g. water per 100 ml. solution) was reduced by potassium metal (4 g. per 100 ml. solution) in a closed system under nitrogen. Aqueous solutions of the solid formed were prepared and titrated with potassium dichromate. Under the conditions described 55% of the potassium perrhenate reacted to form potassium rhenide.

When an aqueous solution of the solid mixture of potassium hydroxide and potassium rhenide is treated with thallous ion, a white precipitate, presumed to be thallous rhenide forms. This rapidly decomposes to thallium metal and perrhenate ion.

II. ELECTROCHEMICAL STUDIES

The oxidation states to which perrhenate ion is reduced under various conditions can be determined from polarographic waves by means of the Ilkovic equation,

$$\frac{id}{c} = 607\ n\ D^{\frac{1}{2}}\ m^{\frac{2}{3}}\ t^{\frac{1}{6}}$$

where id is the diffusion current (microamperes), D is the diffusion coefficient ($cm.^2\ sec.^{-1}$), c is the concentration (millimoles per liter) of the reducible substance, m is the rate of flow of mercury from the dropping electrode ($mg.\ sec.^{-1}$), t is the drop time (sec.), and n is the number of electrons involved in the reduction.

Lingane (9) found that perrhenate in 2-4 N hydrochloric acid solution reduces to Re(IV). In neutral unbuffered solutions containing 2 N potassium chloride a double wave is produced. The first part of this wave ($E_{\frac{1}{2}}$ = 1.41 v. vs. S.C.E.) is due to the reduction to the rhenide ion. The data in Table III verify the eight-electron reduction. From the Ilkovic equation the theoretical value of id/c for n = 8, corresponding to the reduction of perrhenate to rhenide ion, is 40.3 microamperes/millimole/liter for the particular capillary used.

TABLE III

Diffusion Current of Perrhenate Ion as a Function of Concentration in 2 N Potassium Chloride.

ReO_4^- millimolar	id Microamperes	id/c Microamperes/millimol/liter	
0.0192	0.97	50.5	
0.0487	2.38	48.8	
0.0703	3.39	48.3	
0.192	7.85	40.9	
0.311	12.5	40.2	(Theor. (n=8)=40.3)

Rulfs and Elving (10) also found that the first reduction wave of perrhenate in 4 N hydrochloric acid is a three-electron reduction. To confirm that the reduction product is (ReIV), they prepared potassium hexachlororhenate (IV) and found that it reduced at a potential in good agreement with the double reduction wave of the perrhenate ion. The eight-electron reduction at -1.41 volts in neutral solution reported by Lingane (9) was confirmed.

Geyer (11) has measured the half-wave potentials of the steps in the reduction of perrhenate in neutral, alkaline, and acid solutions. In alkaline, neutral, and very weak acid solution, he believes that the reaction proceeds in the steps

$$\mathrm{Re(VII)} = \mathrm{Re(0)} - \mathrm{Re(-I)}$$

In high acid concentration, he finds three waves corresponding to the reduction steps

$$\mathrm{Re(VII)} - \mathrm{Re(IV)} - \mathrm{Re(0)} - \mathrm{Re(-I)}$$

The waves obtained from the reduction of perrhenate ion are very poorly defined, and Geyer has chosen to interpret a slight inflection in the wave as the reduction to Re(0). However, his results are in fair agreement with the results of previous investigators.

Lingane (3) investigated the oxidation of the rhenide ion at the dropping mercury electrode. The oxidation process is described by the five steps listed in Table IV.

TABLE IV

Stepwise Oxidation of Rhenide Ion at the Dropping Mercury Electrode

Step	Reaction	$E_{\frac{1}{2}}$, volts vs. saturated calomel electrode
α	$Re^- \rightarrow Re^{++} + 3e^-$	-0.54
β', β"	$Re^{++} \rightarrow Re^{+++} + e^-$	
γ	$Re^{+++} \rightarrow Re^{+5} + 2e^-$	-0.34
δ	$Re^{+5} \rightarrow Re^{+7} + 2e^-$	-0.07
	Mercury dissolution	----

That Re(II) is the first oxidation product is not substantiated by the chemical evidence given above.

Lingane (3) suggests that since rhenium (0) has the ground state configuration,

$$5s^2 5p^6 5d^5 6s^2$$

one might expect either of the following configurations for the rhenide ion:

A. $5s^2\ 5p^6\ 5d^6\ 6s^2$ B. $5s^2 5p^6 6s^2 6p^6$

Since the rhenide ion has halide-like character, Lingane suggests that configuration B is the more likely. This configuration requires the promotion of all 5d electrons and makes for instability. (Pauling (12) proposes that the structure of Re(-I) is like platinum(II) with four coordinated water molecules at the corners of a square.)

The oxidation of the rhenide ion has also been studied polarographically by Rulfs and Elving (13). Although these investigators obtained five steps in the anodic wave, they believe the first oxidation product to be Re(I). They further postulate that the oxidation of Re(-I) to Re(I) is thermodynamically reversible. On the basis of this postulation, Rulfs and Elving present evidence for the ability of the rhenide to form complexes. In hydrofluoric acid medium the half-wave potential for the first step is -0.426 volts, but more negative values are obtained in the presence of chloride, bromide, iodide, hydrochloric acid-pyridine, hydrochloric acid-thiocyanate, and ethylenediamine, indicating that the reductions proceed with greater difficulty.

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HALOGEN CATIONS

L. H. Diamond November 18, 1952

Introduction:

The electronegativity of the halogens is continually stressed, and it is pointed out that the chlorine atom, having the greatest affinity for electrons, can displace bromine and iodine from solutions of their salts. The electropositive character of the halogens, however, is frequently overlooked. The electropositivity of the halogens increases with increasing atomic number, and the resultant positive character can be observed either in the polarization or polarizability of halogen compounds in which a positive charge becomes centered on the halogen atom, or in the ability of the halogen to form positive ions. With chlorine, electropositive character amounts to little more than measurable polarity in covalent bonds. With iodine, however, electropositive character is so increased that positive iodine ions can exist in simple or complex compounds. Studies of the chemical properties of astatine by tracer techniques indicate that the trend would probably extend to this element (1). The subject of positive halogens has recently been reviewed by Reeve (2).

Trivalent Iodine:

Partington and Bahl (3) observed that ozone will convert iodine into a compound I_4O_9, or $I(IO_3)_3$. This same compound has been prepared by the treatment of iodic acid with phosphoric acid (4). Ficter and Stern (5) prepared $I(C_2H_3O_2)_3$ by oxidizing iodine with fuming nitric acid in the presence of acetic anhydride. From the respective halogenated acetic acids, $I(CH_2ClCO_2)_3$ $I(CHCl_2CO_2)_3$, $I(CCl_3CO_2)_3$, and $I(CH_2BrCO_2)_3 \cdot I(IO_3)_3$ are obtained whereas in the presence of phosphoric acid the normal phosphate IPO_4 is formed. These compounds are unstable and hydrolyze in accordance with the equations of the type:

$$5IPO_4 + 9H_2O \rightarrow I_2 + 3HIO_3 + 5H_3PO_4$$

When a saturated solution of iodine triacetate in acetic acid is electrolyzed, iodine is quantitatively liberated at the cathode. The cation I^{+++} reacts with aromatic nuclei in the following manner;

$$I^{+++} + RH \rightarrow RI^{++} + H^+$$

$$I^{+++} + 2RH \rightarrow R_2I^+ + 2H^+$$

Univalent Halogens:

The treatment of a solution of iodine in a non-aqueous solvent such as chloroform with silver perchlorate or acetate

forms the unstable salts $IClO_4$ and $IC_2H_3O_2$ (6). When silver nitrate is added to an alcoholic solution of iodine, INO_3 is formed.

Kikindai and coworkers (7) have recently indicated the possibility of the fixation of the cation Br^+ and I^+ by the cationic exchanger Amberlite IR100H. Using a solution of iodine or bromine in absolute alcohol, Kikindai was able to prepare solutions of compounds of Br^+ and I^+. A typical procedure was to pass a solution of 0.5 g. of iodine in 100 ml. of absolute alcohol through the Amberlite IR100H.

$$H^+Res^- + I_2 \rightarrow I^+Res^- + HI$$

The formation of HI caused a measurable decline in the pH of the solution. The amount of positive iodine in the resin was determined by passing a saturated solution of KI through the exchange column and titrating the liberated iodine with thiosulfate.

$$I^+Res^- + KI \rightarrow K^+Res^- + I_2$$

Approximately 0.02-0.03 grams of I^+ can be fixed upon the resin by this method, and solutions of I_2SO_4 and INO_3 were obtained by passing a solution of H_2SO_4 and HNO_3 in absolute alcohol through the exchanger containing the positive I^+ ion. With this procedure, the salts of positive iodine and bromine can be prepared from the corresponding acid if the solutions are completely anhydrous and the activity of the H^+ ion is great enough to effect the change.

I^+ may be stabilized by coordination with pyridine, and the resulting compounds may be isolated in the crystalline state. Audrieth and Birr (8) postulated the formation of $I(py)^+$ from conductivity measurements of solutions of iodine in pyridine, and Kleinberg (9) has presented spectrophotometric evidence for the existence of $I(py)^+$ in solutions of iodine in pyridine.

Carlsohn (10,11,12) prepared a series of salts of the hypothetical bases $I(py)OH$ and $I(py)_2OH$. These salts are prepared by treating the silver or mercury salt of the necessary acid with the calculated amount of iodine and a slight excess of pyridine in a solvent such as chloroform, according to the equation:

$$AgAn + py + I_2 \rightarrow I(py)An + AgI$$

Crystalline compounds prepared include $I(py)NO_3$, $I(py)_2NO_3$, $I(py)_2ClO_4$, $I(py)_2C_2H_3O_2$, and a series of $I(py)^+$ salts of some thirty organic acids prepared by Kleinberg et al (13). The chemical reactions of the salts indicate the halogen is positive and univalent. When dissolved in sodium hydroxide containing potassium iodide and then acidified, they all liberate free iodine.

The reactions of $I(py)_2NO_3$ are summarized below. The other salts behave similarly.

1. The iodi-pyridine salts hydrolyze slowly in water.

$$I(py)_2NO_3 + HOH \rightarrow I(py)OH + py \cdot HNO_3$$

$$5I(py)OH \rightarrow 2I_2 + py \cdot HIO_3 + 2H_2O + 4py$$

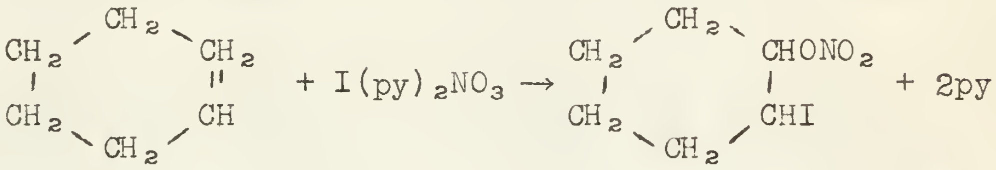
2. Upon treatment with sodium hydroxide the bases $I(py)OH$ and $I(py)_2OH$ are liberated. These immediately revert to their respective anhydrides, which can be isolated.

$$2I(py)_2OH \rightarrow I(py)\text{-}O\text{-}I(py) + HOH$$

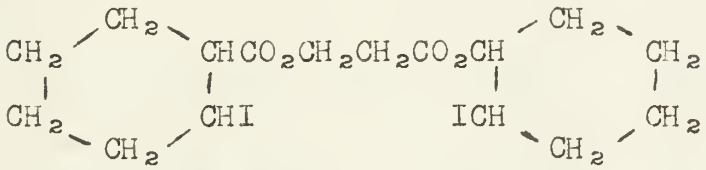
3. The salts of iodine react immediately with phenol to produce the iodophenols.

$$C_6H_5OH + 3I(py)_2NO_3 \rightarrow C_6H_2I_3OH + 3HNO_3 + 6py$$

4. The salts of the halogens are fixed by addition to a double bond.



In the case of an iodine salt with bivalent anions, as in the case of iodine succinate reacting with cyclohexene, the following product is obtained (14).



5. The salts of iodine in a chloroform solution will dissolve the noble metals.

$$3I(py)_2NO_3 + Au \rightarrow Au^{+++} + 3NO_3^- + 3/2\ I_2 + 6py.$$

This confirms Finklestein's conclusion that the I^+ ion should be placed with the noble metal ions in the electromotive series (14).

6. Electrolysis of $I(py)_2NO_3$ in chloroform or methanol produces iodine at the cathode.

Methyl substituted pyridines such as β-picoline, 2-6-lutidine, 2-4-lutidine, and 2-4-6-collidine yield similar I^+ compounds. By similar procedures the bromine compounds $Br(py)_2NO_3$ and $Br(py)_2ClO_4$ and the chlorine compound $Cl(py)_2NO_3$ have been prepared.(15,16)

Evidence for the existence of a unipositive bromine cation is advanced from studies of the brominating strength of solutions of aqueous bromine, alkaline hypobromite, and acid HOBr(17,18). The relative brominating power observed experimentally is acid HOBr ≫ bromine > alkaline OBr^-. The enhanced brominating strength of acid HOBr results from the formation of a positive bromine cation.

$$HOBr + H^+ \rightarrow Br^+ + H_2O \quad \text{and}$$
$$HOBr + H^+ \rightarrow (H_2OBr)^+$$

Attempts to prove the existence of cationic bromine in acidified hypobromous acid solutions by electrolysis have not been completely successful (18). The existence of Cl^+, probably in the form of $(H_2OCl)^+$ has been recently deduced from studies of the chlorinating power of acid solutions of hypochlorous acid (20). The hydrated form of Cl^+ is not formed at as low acidities as $(H_2OBr)^+$, since HOCl is a weaker base than HOBr by a factor of 10^4.

With fluorine electropositive character is reduced to a minimum; however, Cady (21,22) has prepared some so-called "hypofluorites", FNO_3 and $FClO_4$. These are gaseous compounds in which the fluorine is linked by a covalent bond to oxygen. Fluorine in the "hypofluorites" has a valence of +1, but there is little likelihood that any ionic forms of the acid or its derivatives will ever be isolated because of the covalent nature of the molecular bonds.

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REACTIONS OF THE NITROSYL ION

M. K. Snyder

November 25, 1952

A. Introduction

In 1909, Hantzsch suggested the existence of the nitrosyl ion, NO^+, when he obtained anomalously low values for the cryoscopically determined molecular weight of nitrosyl sulfuric acid (12). Later, the existence of the nitrosyl ion was proved by Angus and Leckie (7) who studied the Raman spectra of nitrosyl sulfuric acid. Recently, Addison and coworkers (5) and Partington and Whynes (18) investigated dinitrogen tetroxide. They concluded that in certain instances dinitrogen tetroxide reacts as though it were nitrosyl nitrate.

Addison recognized that dinitrogen tetroxide can dissociate in three ways:

$$N_2O_4 \rightleftharpoons NO_2 + NO_2$$

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

The first of these dissociations is the familiar thermal reaction. The second represents the apparent way in which dinitrogen tetroxide reacts with covalent compounds, such as organic amines. The third shows the type of dissociation involved when dinitrogen tetroxide reacts with ionic compounds, such as amine hydrochlorides. Actually, Angus, Jones, and Phillips (6) have shown that the liquid dinitrogen tetroxide does not undergo self-ionization. Rather, they picture the molecule in a polarized state, such that under the proper environmental conditions it reacts as though it were ionized.

For the sake of convenience, a solvent system may be developed using dinitrogen tetroxide as the solvent and considering it to be nitrosyl nitrate. In this way the reactions of nitrosyl compounds may be classified in a familiar manner.

B. Neutralization

In the nitrosyl nitrate system, the nitrosyl ion is the acidic species and the nitrate is the basic species. When a nitrosyl halide reacts with a nitrate, nitrosyl nitrate is produced, along with a metallic halide.

$$M(NO_3)_x + xNOCl \rightarrow MCl_x + xNONO_3$$

This reaction has been run for the chlorides of zinc (4), silver (5), thallium (17) and lead (18).

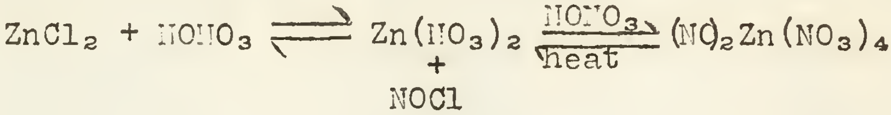
C. Solvolysis

Addison, Conduit, and Thompson (3) have shown that amine hydrochlorides undergo normal solvolysis with nitrosyl nitrate to give the amine nitrates and nitrosyl chloride, according to the equation

$$R_4NCl + NONO_3 \rightarrow R_4NNO_3 + NOCl$$

The reaction takes place when R is methyl, ethyl, methyl and hydrogen, or ethyl and hydrogen. This is a good method for the preparation of the amine nitrates.

Certain metal nitrates are difficult to prepare in the anhydrous state. If the chloride undergoes solvolysis with nitrosyl nitrate, this affords a relatively easy method for the preparation of the anhydrous nitrates. Addison and coworkers (3) have worked this out for anhydrous zinc nitrate:



$$ZnCl_2 + NONO_3 \rightleftharpoons \underset{\displaystyle NOCl}{\underset{+}{Zn(NO_3)_2}} \xrightarrow[heat]{NONO_3} (NO)_2Zn(NO_3)_4$$

As the equation indicates, the end product is actually the complex dinitrosyl tetranitrato zincate(II), which decomposes to the nitrate upon heating. A similar reaction with titanium tetrachloride was not very successful due to undefined side-reactions (18).

The most commonly applied hydrolysis reaction takes place in the Glover tower of the lead chamber process for the production of sulfuric acid (30). The reactions take place as follows:

$$2SO_2 + NO + NO_2 + H_2O + O_2 \rightarrow 2NOHSO_4$$

$$2NOHSO_4 + H_2O \rightarrow NO + NO_2 + 2H_2SO_4$$

The first step of the hydrolysis of the nitrosyl sulfuric acid probably produces nitrous acid, i.e. $NO \cdot OH$ which, in the presence of acid, decomposes into nitric oxide and nitrogen dioxide.

The acid salts of diethyl amine undergo solvolysis to give diethyl nitrosamine (3).

$$(C_2H_5)_2NH \cdot HNO_3 + NONO_3 \rightarrow (C_2H_5)_2N\text{-}NO + 2HNO_3$$

$$(C_2H_5)_2NH \cdot HCl + NOOH \rightarrow (C_2H_5)_2N\text{-}NO + HCl + H_2O$$

$$(C_2H_5)_2NH \cdot HNO_3 + NOCl \rightarrow (C_2H_5)_2N\text{-}NO + HCl + HNO_3$$

D. Solvation and Desolvation

Addison and Conduit (1,2) have shown that the diethyl nitrosamine will solvate the nitrosyl ion.

$$NONO_3 + (C_2H_5)_2N\text{-}NO \rightarrow [NO \cdot 2(C_2H_5)_2N\text{-}NO]NO_3$$

$$(NO)_2Zn(NO_3)_4 + (C_2H_5)_2N\text{-}NO \rightarrow [NO \cdot 2(C_2H_5)_2N\text{-}NO]_2Zn(NO_3)_4$$

Although they realized that they were able to prepare nitrosyl compounds, the early investigators did not know the exact nature of these compounds. As a result, they reported them as addition compounds:

$$M_xX_y + rNOX \rightarrow M_xX_y \cdot rNOX$$

At the present, such compounds are usually written as coordination compounds:

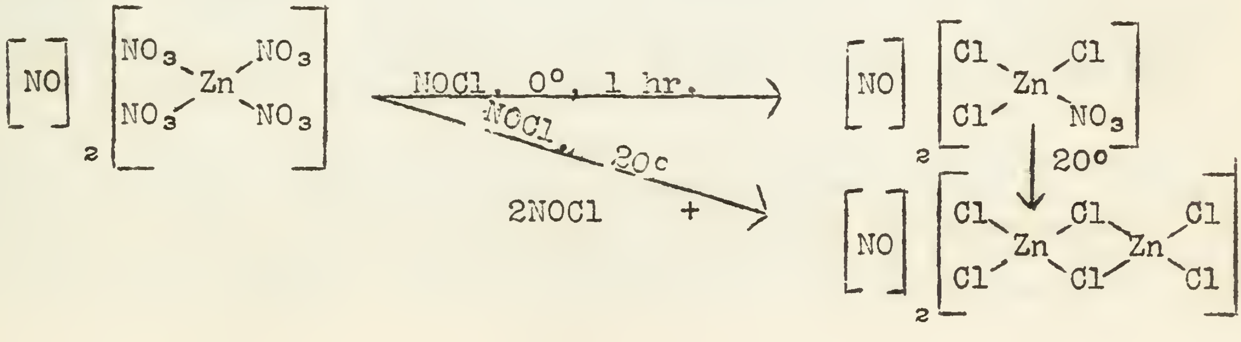
$$M_xX_y + rNOX \rightarrow (NO)_rM_xX_r + y$$

Many of the complex halides of metals have been prepared in this manner, using the appropriate nitrosyl halide. Table I lists these compounds with the metal salt from which they were derived.

Table I

M_xX_y	Old Notation	New Notation	Investigators
$AlCl_3$	$AlCl_3 \cdot NOCl$	$NOAlCl_4$	11,17,18
AsF_5	$AsF_5 \cdot NOF$	$NOAsF_6$	20
$CuCl$	$CuCl \cdot NOCl$	$NOCuCl_2$	8,9,17
$FeCl_3$	$FeCl_3 \cdot NOCl$	$NOFeCl_4$	17,27
$GaCl_3$	$GaCl_3 \cdot NOCl$	$NOGaCl_4$	17
$HgCl_2$	$HgCl_2 \cdot NOCl$	$NOHgCl_3$ $[(NO)_2Hg_2Cl_6]$	17
$InCl_3$	$InCl_3 \cdot NOCl$	$NOInCl_4$	17
$MnCl_2$	$MnCl_2 \cdot NOCl$	$NOMnCl_3$ $[(NO)_2Mn_2Cl_6]$	8,17
PF_5	$PF_5 \cdot NOF$	$NOPF_6$	14
$PdCl_2$	$PdCl_2 \cdot 2NOCl$	$(NO)_2PdCl_4$	18
$PtCl_4$	$PtCl_4 \cdot 2NOCl$	$(NO)_2PtCl_6$	18,27
$SbCl_5$	$SbCl_5 \cdot NOCl$	$NOSbCl_6$	22
SbF_5	$SbF_5 \cdot NOF$	$NOSbF_6$	8
$SnCl_4$	$SnCl_4 \cdot 2NOCl$	$(NO)_2SnCl_6$	17,27
$TiCl_4$	$TiCl_4 \cdot 2NOCl$	$(NO)_2TiCl_6$	17
$TlCl_3$	$TlCl_3 \cdot NOCl$	$NOTlCl_4$	17,27
$ZnCl_2$	$ZnCl_2 \cdot NOCl$	$NOZnCl_3$ $[(NO)_2Zn_2Cl_6]$	17,27

Some of the modern notations in Table I indicate odd coordination numbers. The alternative structures in brackets are suggested on the basis of a desolvation reaction studied by Addison and Lewis (4). Their work may be illustrated by the following scheme:



In the light of these reactions, it seems likely that the zinc, mercury, and manganese compounds in Table I are actually the dimers.

E. Other Metathesis Reactions

In certain instances, dinitrogen trioxide reacts like a nitrosyl compound. From inspection, it may be called either nitrosyl nitrite or nitrosyl oxide. Either formulation will predict the products of the reactions with selenic acid (15), tetrafluoroboric acid (9,28), and fluorosulfonic acid (13).

Woolf (29) carried out some reactions in liquid bromine trifluoride which undergoes self-ionization:

$$2BrF_3 \rightarrow BrF_2^+ + BrF_3 \cdot F^-$$

Typical reactions take place with metal compounds and nitrosyl chloride in bromine trifluoride:

$$M_xX_y + rBrF_3 \rightarrow xMF_{\frac{r}{x}} + \frac{r}{x}(BrF_2)_xX$$

$$NOCl + BrF_3 \rightarrow NOF + BrF_2Cl$$

$$zNOF + MF_{\frac{r}{x}} \rightarrow NOMF_{\frac{r}{x}} + z$$

Table II shows a few of the complex compounds which Woolf has prepared in this way.

Table II

Reactant	Product
NOX →	
$SnCl_4$	$(NO)_2SnF_6$
As_2O_3	$NOAsF_6$
Sb_2O_3	$NOSbF_6$
B_2O_3	$NOBF_4$
PBr_5	$NOPF_6$
GeO_2	$(NO)_2GeF_6$
SnF_4	$(NO)_2SnF_6$
SiO_2	$(NO)SiF_6$
$(NO)_2S_2O_7$	$NOSO_3F$

In addition it was found that it is possible to replace the coordinated chlorides in a complex compound with fluoride by treating the complex with bromine trifluoride. So if a metal such as gold is dissolved in nitrosyl chloride to give nitrosyl tetrachloro-aurate(III), treatment with bromine trifluoride produces nitrosyl tetrafluoro aurate(III).

In Germany, Seel and coworkers have prepared nitrosyl compounds in liquid sulfur dioxide, a non-solvolytic solvent for these reactions (22). By combination of tetramethyl ammonium nitroprussate and nitrosyl hexachloroantimonate(V), they have obtained a mixture of nitrosyl tetramethyl ammonium nitroprussate and

dinitrosyl nitroprussate (26). Using the same starting nitrosyl compound with tetramethyl ammonium hexafluophosphate, they obtained the nitrosyl hexafluophosphate without having to handle nitrosyl fluoride or bromine trifluoride (24).

F. Oxidation-Reduction

Active metals will react with water to produce hydrogen and a base. In a similar fashion zinc (4), the alkali metals (6), mercury (5), and copper (5) will react with nitrosyl nitrate to produce the metal nitrate and nitric oxide. If an acid, such as nitrosyl chloride, is used, in addition to these metals, iron (5), tin (5), thallium (5), indium (5), gallium (5), gold (18), and platinum (18) will react.

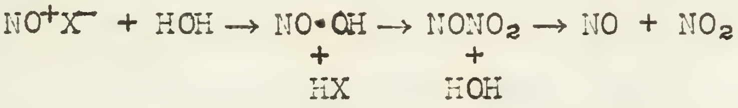
The intensity of the color of nitrosyl halides increases as the size of the halide increases. In the same way, the degree of dissociation of the halides increases with increasing size of the halide. In fact, nitrosyl iodide has never been prepared. Seel and coworkers (23) have investigated the reaction of nitrosyl compounds with iodides. In all cases the liberation of free iodine was observed:

$$2NOX + 2KI \rightarrow NO + \tfrac{1}{2}I_2 + 2KX$$

KI could be any convenient iodide. They found, also, that the presence of a very slight number of nitrosyl ions could be detected in this way. Even ethyl nitrite, which didn't react itself, did react when dissolved in acidic solvents such as sulfur dioxide, sulfur trioxide, boron trichloride, or hydrogen chloride. This reaction may serve as a test for the nitrosyl group.

Similarly, Seel and coworkers (25) studied the reactions of nitrosyl compounds with azides. Instead of the very unstable nitrosyl azide, they obtained nitrogen and nitrous oxide. Likewise, this reaction can serve as a test for the nitrosyl group.

Seel (21) found that the salt like nitrosyl compounds reacted violently with water to produce nitric oxide and nitrogen dioxide. This reaction proceeded according to the equation:



$$NO^+X^- + HOH \rightarrow \underset{\substack{+\\ HX}}{NO\cdot OH} \rightarrow \underset{\substack{+\\ HOH}}{NONO_2} \rightarrow NO + NO_2$$

However, it was found that the coordinated nitrosyl group in nitrosyl nitroprussate did not react in this way.

G. Summary

Assuming the existence of the nitrosyl ion and the ability of dinitrogen tetroxide, dinitrogen trioxide, and nitrous acid to dissociate into nitrosyl ions, the typical reactions of a solvent system allow systematization of the preparation of nitrosyl salts, complex nitrosyl compounds, and certain anhydrous inorganic nitrates. Oxidation-reduction reactions serve as a means to detect the presence of the nitrosyl group in its ionic form as well as its covalent form.

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THE OCCURRENCE OF MAXIMUM OXIDATION STATES AMONG THE FLUOROCOMPLEXES OF THE FIRST TRANSITION SERIES

D. H. Busch November 25, 1952

Introduction

In his book on unfamiliar oxidation states, Kleinberg (1) states that the potentialities of fluorine as an oxidizing agent for the study of higher oxidation states have scarcely been tested. The implications of this statement are emphasized by the studies under consideration here. The higher of the normal oxidation states of an element commonly occur in combination with fluorine. (2) This is illustrated in Table 1 which lists the binary fluorides of the elements of the first transition series. (3)

Table 1

			CrF_2	MnF_2	FeF_2	CoF_2	NiF_2	CuF_2	ZnF_2
ScF_3	TiF_3	VF_3	CrF_3	MnF_3	FeF_3	CoF_3			
	TiF_4	VF_4	CrF_4						
	VF_5								

Binary Fluorides of the First Transition Series.

The tetra and pentafluorides of vanadium and the tetrafluoride of chromium are quite significant in pointing out this relationship.

The highest valencies so far obtained for many of these elements are associated with the formation of oxy-anions. In these compounds the dual effects of the presence of oxide ions, which are difficult to oxidize, and the formation of complex ions are both operative. It is then to be expected that fluorocomplexes can be prepared in which high valence states are associated with the central metal atoms. The highest valence states known in fluorocomplexes prior to the work to be discussed here are summarized in Fig. 1. The maximum valence states which have been observed for these elements in oxycomplexes are shown in Fig. 2.

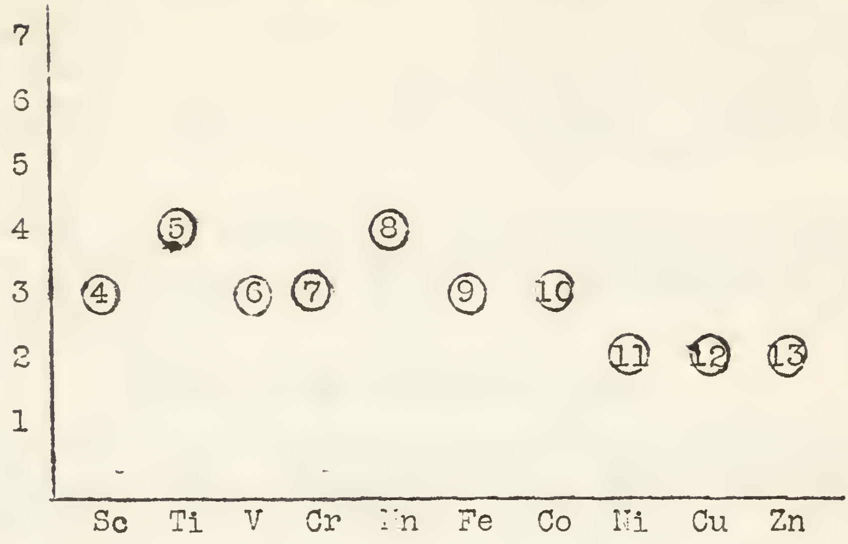


Fig. 1

The maximum valencies found in fluorocomplexes of the transition elements as of 1948. The circled number gives the reference as listed in the bibliography.

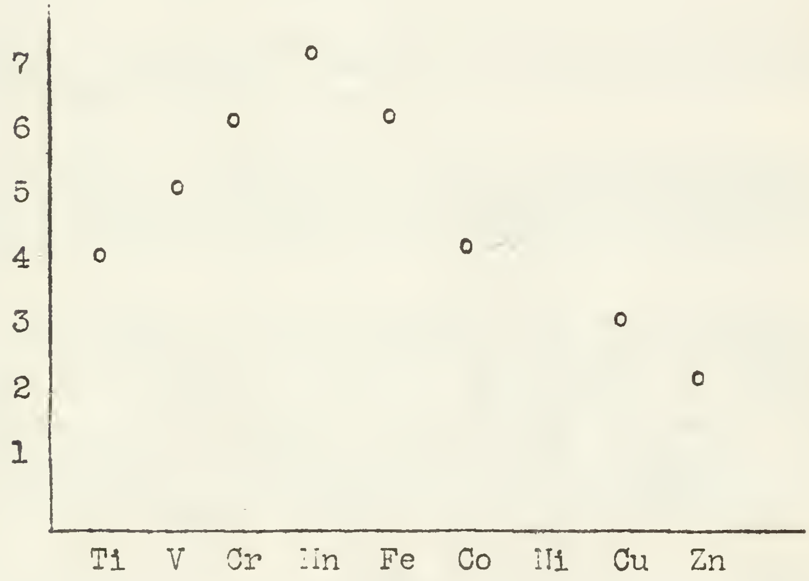


Fig. 2

The maximum valencies found in oxy-complexes of the transition elements.

Preparation of Fluorocomplexes Containing Central Atoms of High Valence

Klemm and Huss (2,14) prepared fluorocomplexes of the elements vanadium through copper by fluorination of mixtures of potassium chloride and the chloride of the appropriate metal. In each case the molar ratio of potassium chloride to transition metal chloride was varied until a homogenous product was obtained. Each product was then characterized by analysis, weight change during fluorination, and by x-ray and chemical means.

Red potassium hexafluoronickelate(IV) (K_2NiF_6) prepared in this manner was found to be isomorphous with potassium hexafluorosilicate (2). It is hydrolyzed by water, and reduced by hydrogen according to the equation

$$K_2NiF_6 + H_2 \rightarrow K_2NiF_4 + 2HF$$

With copper (2) a pale green complex of the composition K_3CuF_6 was obtained. This compound is also decomposed by water. Hydrogen reduction produces copper(I) fluoride.

In the case of cobalt, (2) bright blue potassium heptafluorocobaltate(IV) (K_3CoF_7) was prepared. This substance is isomorphous with K_3ZrF_7. It is fairly stable toward reduction by hydrogen; however, at 450° it is slowly converted to potassium hexafluorocobaltate(III).

$$K_3CoF_7 + \tfrac{1}{2}H_2 \rightarrow K_3CoF_6 + HF$$

Potassium heptafluorocobaltate(IV) reacts with water releasing only a small part of its fluorine.

Fluorination of iron salts produced only a trivalent hexafluoroferrate(III) complex(2) which was found to be identical with the product obtained by a wet method.

The only product obtainable by the method of Klemm and Huss with manganese (14) was potassium hexafluoromanganate(IV) (K_2MnF_6). This product was identical with that obtained by Weinland and Laurenstein (5).

Similar experiments with chromium (14) were complicated by the formation and volatilization of chromium(V) fluoride. With the molar ratio of 2 KCl to 1 $CrCl_3$, the amount of chromium lost by volatilization was a minimum, and yellow potassium hexafluorochromate(IV) (K_2CrF_6) was found in the solid residue. Potassium hexafluorochromate(IV) is isomorphous with potassium hexafluoromanganate(IV). When heated in the presence of hydrogen, the chromium disproportionates with the result that volatile chromium (V) fluoride sublimes away, leaving behind green potassium hexafluorochromate(III).

$$2K_2CrF_6 \xrightarrow[\Delta]{} CrF_5 + K_3CrF_6 + KF$$

The same reaction occurs in an atmosphere of nitrogen although it does not proceed to completion at 300°.

Difficulties similar to those associated with the chromium compound were encountered with vanadium (14). At reaction temperatures in excess of 100° vanadium(V) fluoride sublimes away. The best results were obtained by subjecting the green trivalent complex K_2VF_5 to fluorination. The nearly colorless product of the fluorination reaction had the composition K_2VF_6. The potassium pentafluorovanadate(III) was prepared (6) by the addition of potassium fluoride to a solution of vanadium(III) fluoride in anhydrous hydrogen fluoride.

Emeleus and Gutmann (15) succeeded in preparing the potassium, barium and silver salts of the hexafluorovanadate(V) ion by the reaction of vanadium(III) chloride and potassium chloride in anhydrous bromine trifluoride. Potassium hexafluorovanadate(V) (KVF_6) was also prepared by the reaction of potassium fluoride with vanadium(V) fluoride in a sealed tube. These salts fume in air liberating hydrogen fluoride and vanadium(V) oxide. KVF_6 is decomposed in vacuo at 330°.

Two tetravalent fluorocomplexes of manganese were prepared by Sharpe and Woolf. (16) The reaction of potassium permanganate with the solvent bromine trifluoride produced the pink salt, potassium pentafluoromanganate(IV). The x-ray pattern of this product showed that no potassium fluoride, manganese(III) fluoride, or potassium hexafluoromanganate(IV) was present. $KMnF_5$ reacts with water liberating manganese(IV) oxide, hydrogen fluoride, and potassium fluoride. Yellow potassium hexafluoromanganate(IV) was prepared by the reaction of potassium permanganate with bromine trifluoride in the presence of potassium chloride. This product was identical with K_2MnF_6 prepared by a wet method (17).

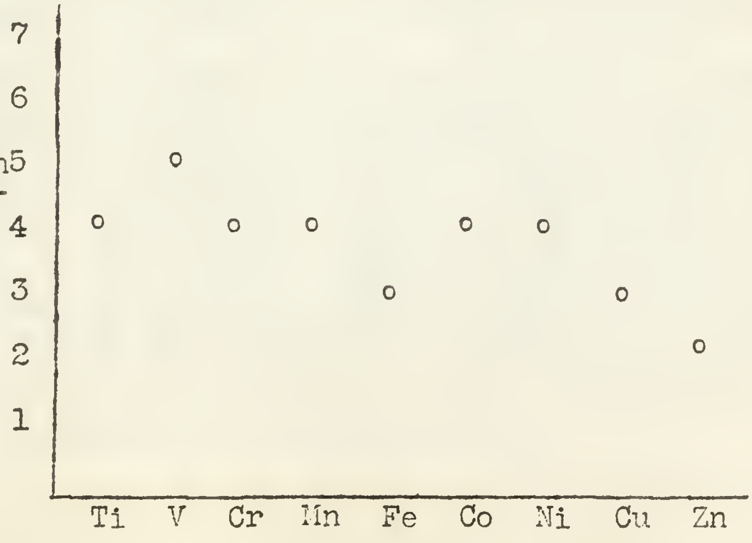
The reaction of chromate ion with bromine trilfuoride (16) produced only mixed oxyfluorocomplexes.

Interpretation of the Experimental Results

The most obvious conclusion that can be drawn from the preceding review is that the higher valence states are not so well stabilized through the formation of fluorocomplexes as might be expected in view of the known oxycomplexes. The highest oxidation states obtained in fluorocomplexes are summarized in Fig. 3.

Fig. 3

The maximum valences known for fluorocomplexes of the elements of the first transition series.



Klemm (18) calculated the heats of reaction for the reactions shown below.

$$3KF + VF_3 \rightarrow K_3VF_6$$

$$2KF + VF_4 \rightarrow K_2VF_6$$

$$KF + VF_5 \rightarrow KVF_6$$

His calculations indicate that, on the basis of electrostatic relationships, the tetravalent complex should be the most stable of the three while KVF_6 should be relatively easy to decompose into vanadium(V) fluoride and potassium fluoride. This is in agreement with the experimental findings.

The failure of investigators to prepare fluorocomplexes in which chromium, manganese, iron, cobalt, and nickel exhibit their maximum known valences (though admittedly an inferior type of evidence for their inability to exist) should lead to a reexamination of the reasons given for expecting such compounds to form. The stabilizing effect on valence state which accompanies complex formation is not the same with fluorine as with many other ligands. This is associated with the fact that the bonds formed between fluorine and the transition elements are primarily of the ionic type (10), so that the stable electronic configurations attainable by the central atom do not involve filling of its electronic orbitals with electrons contributed by coordinating ligands. The stable configurations are, to the contrary, the same as those associated with gaseous atoms, i.e., completely filled, half-filled and empty electronic shells.(2,19) Recognition of this fact facilitates the explanation of the stability of the FeF_6^{-3} ion and the stable existence of the CoF_7^{-3} ion.

The absence of experimental proof for the existence of stable fluorocomplexes in which chromium, manganese, and nickel attain such stable configurations may be interpreted to mean that there is an upper limit to the number of electrons which may be removed from these atoms and placed on associated fluorine atoms (18).

Two factors favor the liklihood of attaining higher valencies with oxycomplexes than with fluorocomplexes. According to Klemm (18), the negative two charge on the oxide ion favors a higher positive charge on the nucleus of the central atom on the basis of electrostatic and space considerations. The electronegativity difference between the average value for the elements of the first transition series and that for oxygen indicates that the corresponding bonds should be about 55% ionic (19). On this basis it is reasonable to expect the formation of bonds in which electron sharing plays an important part so that an upper limit on the oxidation state of the transition element need not be expected on the basis of electrostatic considerations.

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POLY- and METAPHOSPHATES

V. D. Aftandilian December 2, 1952

The dehydration of NaH_2PO_4 yields sodium metaphosphate according to the following scheme:

$$NaH_2PO_4 \xrightarrow{\Delta} Na_2H_2P_2O_7 \xrightarrow{\Delta} NaPO_3$$

Many investigators have prepared metaphosphates by heating mixtures of Na_2HPO_4 or $Na_4P_2O_7$ and an ammonium salt (1). Practically all the known metaphosphates have been prepared by a slight modification of this method (4,5,6), i.e. by changing the ratio of the ammonium salt and the final temperature of the dehydration process. However, this method has not been investigated systematically nor has the exact function of the ammonium salt been elucidated.

Kantzer (2) carried out the reactions of Na_2HPO_4 with NH_4NO_3 using a Chevenard Thermobalance (3) to investigate the intermediate products of dehydration. Typical graphs showing the relationship between mole ratios of NH_4NO_3/Na_2HPO_4, rate of heating and temperature are presented in Figures I, II, III.

In a series of experiments where equal weights of ammonium nitrate and disodium hydrogen phosphate were used Kantzer (2) found the final products of dehydration to be either $Na_4P_2O_7$ or $Na_5P_3O_{10}$, depending on the final temperature and on the rate of heating of the mixture. The weight of the excess NH_4NO_3, decomposed in these experiments, was found to be proportional to the weight of the initial Na_2HPO_4. And for the same weight of disodiumhydrogen phosphate the loss of the excess nitrate, in the case of the formation of $Na_5P_3O_{10}$ and $Na_4P_2O_7$, was found to correspond to the ratio of 2/3. (See table I)

Table I

A Anhydrous Na_2HPO_4 gm	B Loss of x's NH_4NO_3 gm	Final Product	Ratio A/B
0.1517	0.0579	$Na_5P_3O_{10}$	2.6
0.0841	0.0311	"	2.6
0.0795	0.020	$Na_4P_2O_7$	3.9
0.1208	0.030	"	3.9

In order to explain this phenomenon Kantzer postulates that the first product of the reaction must be a metaphosphate. Depending on the final temperature either $Na_4P_2O_7$ or $Na_5P_3O_{10}$ is formed when

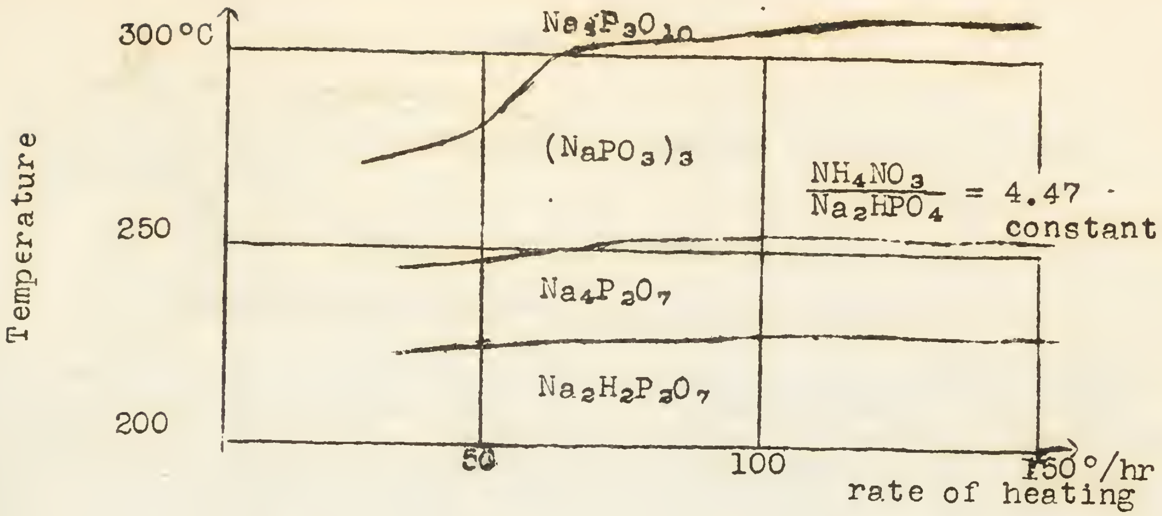
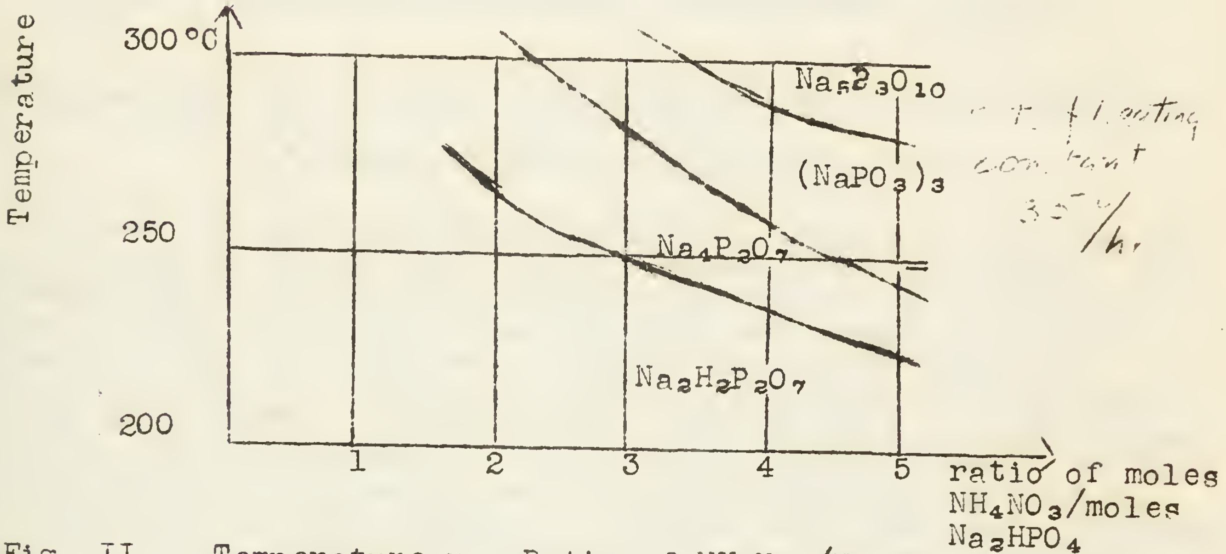


Fig. I Temperature vs. Rate of Heating



rate of heating constant 35°/hr

Fig. II Temperature vs. Ratio of NH_4NO_3/Na_2HPO_4

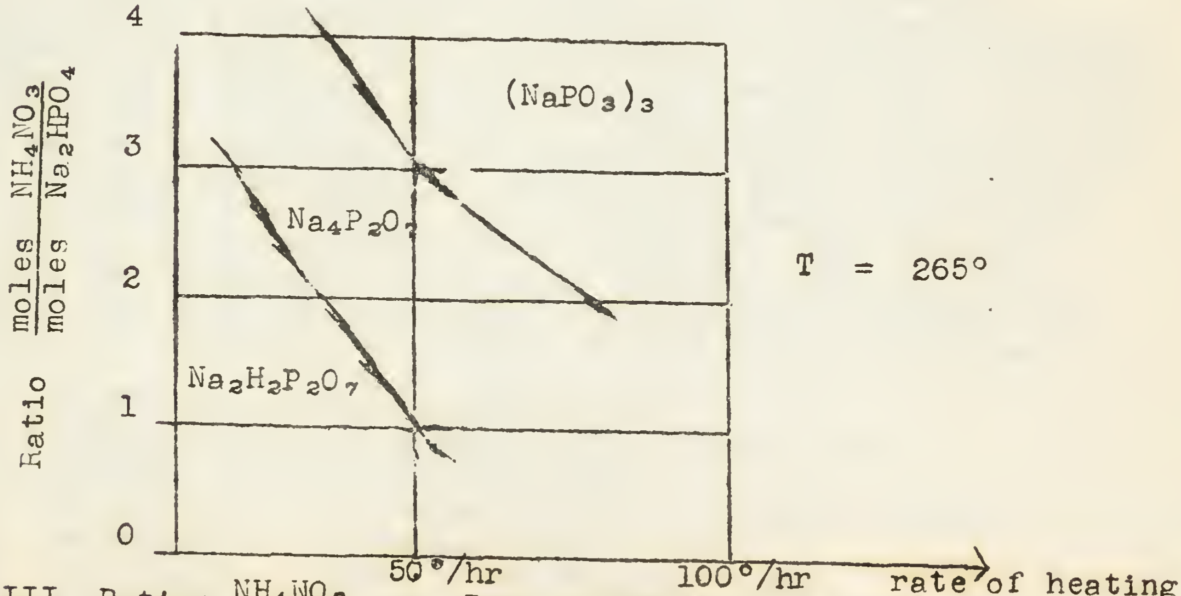


Fig. III Ration $\frac{NH_4NO_3}{Na_2HPO_4}$ vs. Rate of Heating at const. temp.

the metaphosphate reacts with sodium nitrate according to the following equations:

$$(a)\ 2NaPO_3 + 2NaNO_3 \longrightarrow Na_4P_2O_7 + N_2O_5$$

$$(b)\ 3NaPO_3 + 2NaNO_3 \longrightarrow Na_5P_3O_{10} + N_2O_5$$

It is interesting to note that these reactions take place either below or above the region where the trimetaphosphate can exist. (See Figs. I, II and III). Therefore the metaphosphate postulated by Kantzer cannot be the trimer. The metaphosphate, initially formed, is very unstable and reacts with sodium nitrate. If the temperature is kept constant N_2O_5 is said to be evolved(?) and $Na_4P_2O_7$ is the only product of dehydration. But, if the temperature is raised to the domain of the existence of $Na_5P_3O_{10}$ the following reaction could take place:

$$6NaPO_3 + 6NaNO_3 \rightleftharpoons 3Na_4P_2O_7 + 3N_2O_5 \rightleftharpoons 2(NaPO_3)_3 + 6NaNO_3$$

Trimetaphosphate could react with sodium nitrate to give $Na_5P_3O_{10}$.

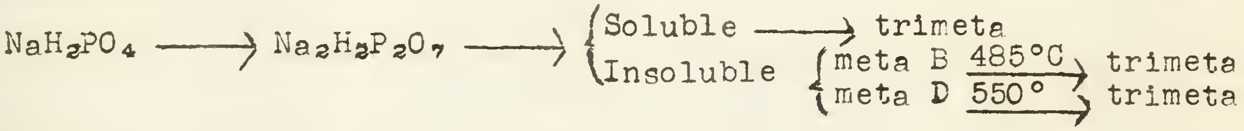
$$3NaNO_3 + 2NaPO_3 \longrightarrow Na_5P_3O_{10} + N_2O_5$$

Kantzer (2) isolated the dehydration product of a mixture of equal weights of Na_2HPO_4 and NH_4NO_3, heated to exactly 236°C. He obtained a yellowish liquid which gave an opaque material when chilled quickly. This was dissolved in a very small quantity of cold water. Oily droplets were formed immediately upon the addition of ethanol. Acetone, dioxane, and carbon tetrachloride gave the same result. The resulting compound gave no precipitate with $AgNO_3$ (characteristic of the ortho phosphate anion). It was found to be very hygroscopic and its density diminished rapidly when exposed to moisture giving a solution which had the characteristics of pyrophosphate. (White precipitate with ethanol). A poorly formed crystalline compound was obtained when it was dried in dry atmosphere. X-ray powder diagram and the infra-red absorption spectra showed that this compound is neither $Na_5P_3O_{10}$ nor $Na_4P_2O_7$. The existence of dimetaphosphate, among the products of dehydration of disodium dihydrogen pyrophsophate was presumably verified by Kantzer (2) by cryoscopic measurements. The reactions of the systems $NaNO_3$-$(NaPO_3)_2$ and $NaNO_3$-$(NaPO_3)_3$ were investigated. For the first of these, $Na_4P_2O_7$ was found at 260°C, $(NaPO_3)_3$ at 270°C, and $Na_5P_3O_{10}$ at 450°C. The second mixture did not react below 300°C., but between 305 - 700°C. $Na_5P_3O_{10}$ was obtained. No $Na_4P_2O_7$ was detected in the second mixture. Taking into consideration the above experimental facts Kantzer (2) summarizes the reactions of Na_2HPO_4 and NH_4NO_3 to take place as follows:

1. $Na_2HPO_4 \cdot aq. \longrightarrow Na_2HPO_4 + aq.$
2. $Na_2HPO_4 + NH_4NO_3 \longrightarrow NaH_2PO_4 + NaNO_3 + NH_3$
3. $2NaH_2PO_4 \longrightarrow Na_2H_2P_2O_7 + H_2O$
4. decomposition and volatilization of excess NH_4NO_3
5. $Na_2H_2P_2O_7 \longrightarrow 2NaPO_3 + H_2O$
6. (a) $2NaPO_3 + 2NaNO_3 \longrightarrow Na_4P_2O_7 + N_2O_5$
   (b) $3NaPO_3 + 2NaNO_3 \longrightarrow Na_5P_3O_{10} + N_2O_5$

Steps 4 and 5 are reversed if the rate of heating is increased.

Boulle (8) investigated the dehydration of NaH_2PO_4 and found that $(NaPO_3)_2$ and an insoluble compound, called Maddrell's Salt, are the dehydration products. He also reported that as the temperature of dehydration is increased the content of Maddrell's Salt is also increased. Investigations carried out on Maddrell's Salt showed that it is composed of two crystalline forms, called B and D by Boulle (8). He summarized his investigations by the following scheme;



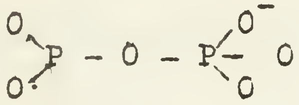
$$NaH_2PO_4 \longrightarrow Na_2H_2P_2O_7 \longrightarrow \begin{cases} \text{Soluble} \longrightarrow \text{trimeta} \\ \text{Insoluble} \begin{cases} \text{meta B} \xrightarrow{485^\circ C} \text{trimeta} \\ \text{meta D} \xrightarrow{550^\circ} \text{trimeta} \end{cases} \end{cases}$$

Partridge, Everett, Hicks and Smith (9) also reported two insoluble forms II and III in Maddrell's Salt and summarized their work as;

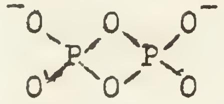
$$NaPO_3III \xrightarrow{400-425^\circ C} NaPO_3II \xrightarrow{475-500^\circ C} NaPO_3\ I \xrightarrow{625^\circ C} \text{fusion}$$

Kantzer (2) studied the infra-red absorption spectra of the various forms of meta-, pyro-, and triphosphate, and found that **certain** bands are common to all these compounds, indicating a close similarity between the structures of these compounds.

Kantzer suggests two possible structures for dimetaphosphate.



(I)



(II)

It is obvious that the second structure could give rise to cis-trans isomerism. The close analogy between the infra-red absorption spectra **and** the X-ray diffraction data of dimetaphosphate and $Na_2H_2P_2O_7$ suggests (I) as a more favorable structure for $(NaPO_3)_2$. This structure also explains the extreme reactivity of this compound since one of the phosphorus atoms lacks a pair of electrons and acts as a Lewis acid. It adds water and many donor groups. Kantzer (2) found that dimetaphosphate decolorizes $Fe(SCN)_3$ but he was not able to isolate the resulting compound.

The author also suggests structure (II) as an explanation for the two isomeric forms, B and D, of Maddrell's Salt. However, he gives no experimental evidence to support this suggestion.

No complexes have been reported for trimetaphosphate.

The tetrametaphosphate can be prepared by allowing hexagonal phosphorus(V) oxide to react with sodium carbonate 10-hydrate (10). The tetramer is capable of forming complexes with heavy metals (11). Kantzer (2) prepared $Fe[Fe(PO_3)_4Cl_2]$ and $Na_3[Fe(PO_3)_4Cl_2]$ by adding a solution of $FeCl_3$ to a solution of tetrametaphosphate.

The structure suggested for this complex is shown in figure I.

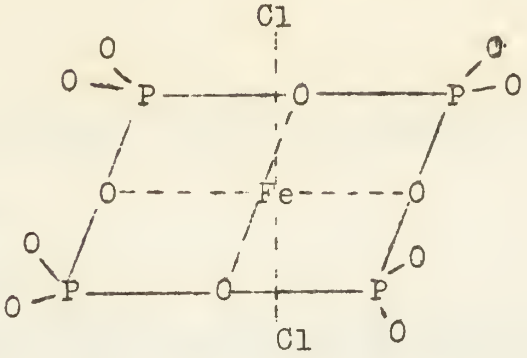


Figure I

Graham's salt, sometimes called hexametaphosphate, is a linear molecule made up of $PO_4^{=}$ tetrahedra linked together by common oxygen atoms. This salt forms complexes. Kantzer (2) prepared the lead complex and by gravimetric analyses established its formula as $Na_2[Pb(PO_3)_4]\cdot 1\frac{1}{2}\ H_2O$. He postulated that the lead (II) ion is capable of breaking the linear chain of this polyphosphate into eight-membered cyclic structures. No structure is suggested by Kantzer for this compound.

Two complexes were prepared from triphosphate and $FeCl_3$ according to the following reactions;

$$Na_5P_3O_{10} + FeCl_3 \longrightarrow Na_3[Fe(P_3O_{10})Cl] + 2NaCl$$

$$Na_5P_3O_{10} + 2FeCl_3 \longrightarrow Fe[Fe(P_3O_{10})Cl] + 5NaCl$$

When a solution of $Fe(NO_3)_3$ is added to a solution of triphosphate a yellowish-white precipitate is formed. Kantzer identified this compound as $Fe_5(P_3O_{10})_3$.

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PRODUCTION OF SILICON CHLORIDES BY ELECTRICAL DISCHARGE AND HIGH TEMPERATURE TECHNIQUES

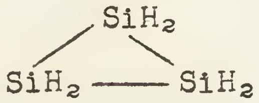
W. E. Cooley December 9, 1952

I. Nomenclature

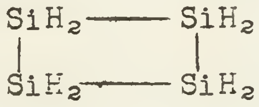
Compounds of the general formula Si_nCl_{2n+2} are known as silanes, and prefixes denote the number of silicon atoms present. (1,3)

SiH_4 ----- silane
Si_2H_6 ---- disilane
Si_3H_8 ---- trisilane, etc.

Cyclic silicon compounds of the general formula $(SiH_2)_n$ are known as cyclosilanes. The number of silicon atoms is denoted as before, always with cyclo- as a first prefix. (1)



---- Cyclotrisilane



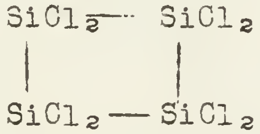
---- Cyclotetrasilane

Halogen derivatives of the silanes are named by prefixing to the name of the parent compound the nature and number of halogen atoms present. (1,6)

SiH_2Cl_2 --- dichlorosilane

Si_2Cl_6 --- hexachlorodilsane

Si_3Cl_8 --- octachlorotrisilane



--- octachlorocyclotetrasilane

II. Early Work

The first production of completely chlorinated silanes by electrical discharge was accomplished by Besson and Fournier in 1908. (2) These investigators subjected a mixture of hydrogen and trichlorosilane vapor to a discharge and obtained an oily liquid product. From the liquid were distilled $SiCl_4$, Si_2Cl_6, and Si_3Cl_8. Si_4Cl_{10} and Si_5Cl_{12} were uncertainly reported as viscous liquids, and Si_6Cl_{14} appeared as a white solid, subliming

at 200°C. in a vacuum. After continued heating in vacuum, a reddish-yellow solid remained. It was thought to be a mixture of higher chlorides, but no further identification was attempted. When tetrachlorosilane was used instead of trichlorosilane, a solid residue again remained after removal of the lower chlorosilanes.

III. More Recent Studies

In 1937 Schwarz and his associates at the University of Königsberg published the first of a series of reports on silicon chlorides of high molecular weights. Schwarz and Heckbach (14) used a so-called "hot-cold" tube for their preparations. A mixtur of tetrachlorosilane vapor and hydrogen gas was admitted into a tube previously filled with an argon atmosphere and fitted with an electrically heated quartz rod. The rod was heated to 1000° - 1100°C. as the gas mixture flowed over it. Condensation and collection of products was accomplished in a flask attached to the hot portion of the tube, the flask being cooled by a liquid air bath. A product mixture was obtained whose more volatile components consisted of $SiCl_4$, $SiHCl_3$, Si_2Cl_6, and HCl. Fractional distillation under high vacuum yielded a very viscous oil boiling at 215°-220°C. The results of analyses and cryoscopic molecular weight determinations led to calculation of the formula $Si_{10}Cl_{22}$. The compound is hydrolyzed vigorously by water, as may be expected for all members of the Si_nCl_{2n+2} series, according to Schumb. (8)

Schwarz and Thiel (16), employing the "hot-cold" tube, substituted a hydrogen atmosphere for the argon atmosphere formerly used. The compound $Si_{10}Cl_{20}H_2$ was separated as a viscous oil. This compound and related chlorinated silanes undergo alkaline hydrolysis in accordance with the following general equations:

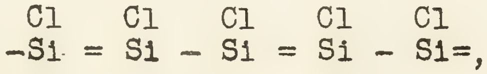
$$(1)\quad Si_nCl_{2n+2} + (4n+2)\,KOH \longrightarrow nK_2SiO_3 + (2n+2)KCl + (n-1)H_2 + (n+2)H_2O$$

$$(2)\quad Si_nCl_{2n}H_2 + 4n\,KOH \longrightarrow nK_2SiO_3 + 2n\,KCl + (n+1)H_2 + nH_2O.$$

Schwarz (10) used the compound $Si_{10}Cl_{20}H_2$ to prepare an amorphous polymerized silicon chloride of empirical formula $(SiCl)_x$. A flask, containing benzene solution of $Si_{10}Cl_{20}H_2$ in a carbon dioxide atmosphere, was attached to a vacuum pump. After all the benzene had been drawn off, the contents were heated to 300°C. The volatile decomposition products, collected in receiver cooled by liquid air, consisted of $SiCl_4$, $SiHCl_3$, Si_2Cl_6, Si_3Cl_8, Si_3Cl_7H, Si_4Cl_{10}, and in some cases hydrogen. A yellow residue remained behind. Hydrolysis of the yellow substance with dilute KOH permitted measurement of the evolved hydrogen. Chlorine was determined titrimetrically, and silicon was determined gravimetrically as SiO_2. Several analyses gave good agreement with a Si:Cl:H ratio of 1:1:3. Such a ratio is in harmony with the general equations for hydrolysis, given above, in that one H_2 molecule is

evolved for each Si-Si bond. The molecular weight of $(SiCl)_x$ could not be determined, because of its insolubility in organic solvents.

Schwarz and Gregor (11) pointed out that the insoluble product $(SiCl)_x$, could not be a mixture of silicon and members of the series Si_nCl_{2n+2}, since benzene or ether would dissolve out the homologs of tetrachlorosilane. No loss of weight was experienced by the yellow material on treatment with solvents; no residue remained behind on evaporation of the solvent. Hydrolysis of a mixture of the above type would leave elemental silicon; actually a pure white, homogeneous hydrolysis product was formed with careful hydrolysis. Furthermore, the yellow material remained unchanged at 400°C. and one atmosphere pressure. A conjugated structure,



$$-\overset{Cl}{Si} = \overset{Cl}{Si} - \overset{Cl}{Si} = \overset{Cl}{Si} - \overset{Cl}{Si}=,$$

was tentatively proposed by the authors; Rochow (7) and Sidgwick (17) have, however, objected to a structure consisting of chains of doubly-bonded silicon atoms.

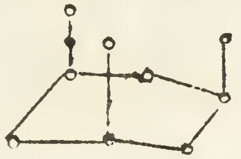
IV. Present Studies

Work in this field is now being carried out by Hertwig and Wiberg (4,5) and Schwarz and Köster. (12,13) Hertwig and Wiberg, working at the University of Munich, have used the glow discharge apparatus of Schwarz and Pietsch. (15) An evacuated tube system was fitted with two aluminum electrodes arranged to produce a glow discharge of 10,000 volts. Hydrogen gas and $SiCl_4$ (or $SiHCl_3$) were admitted at low pressure. It was found that under proper conditions 90-100% of the chloride could be converted to stable materials ranging in composition from $SiCl_{0.5}$ to $SiCl_{2.6}$. Each of the several compositions was found to be reproducible, and quantitative recovery of all products was shown by agreement of stoichiometric calculations with analyses of the non-volatile products. The materials with lowest chlorine content consisted of solid powders; those of higher chlorine content were resinous and oily, and increasingly soluble in benzene and ether. The individual reproducible compositions were apparently often mixtures in themselves, for chlorine-richer components could be dissolved by benzene or ether treatment of chlorine-poorer substances. The following data are based upon the results of cryoscopic determinations.

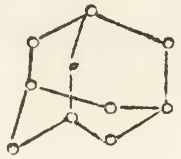
Empirical Formula	Molecular Weight	Proposed Formula
$SiCl_{1.10}$	2555	$Si_{38}Cl_{42}$
$SiCl_{1.27}$	1610	$Si_{22}Cl_{28}$
$SiCl_{1.47}$	1526	$Si_{19}Cl_{28}$
$SiCl_{1.60}$	848	$Si_{10}Cl_{16}$
$SiCl_{2.00}$	891	$Si_{9}Cl_{18}$

Schwarz and Köster have verified the findings of Hertwig and Wiberg by isolating similar materials through the thermal decomposition of $Si_{10}Cl_{20}H_2$ in a stream of argon. By varying the decomposition temperature from 260°C. to 320°C., it was possible to produce chlorides of composition $SiCl_{1.80}$ to $SiCl_{1.18}$.

Hertwig and Wiberg propose for the resulting chlorides a structure composed of sections from the diamond lattice of silicon, with the chlorine atoms occupying the positions necessary to saturate each silicon atom.



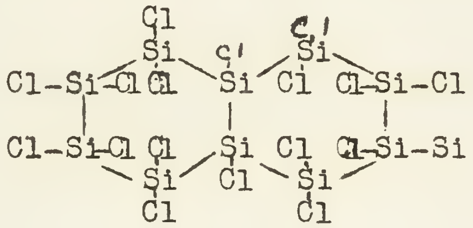
Si_9Cl_{18}, m.w. 891



$Si_{10}Cl_{16}$, m.w. 848

Hydrolysis with KOH is reported to yield a quantity of hydrogen in agreement with the number of Si-Si bonds in these proposed structures.

Schwarz and Köster argue that the amorphous nature of the products precludes any ordered structure such as a diamond lattice. A bicyclic structure is proposed for $Si_{10}Cl_{18}$, for example:



Further condensations, to give products of even higher molecular weight, occur in a random three-dimensional manner, resulting in irregularly interlaced "bundles". As the temperature is increased above 290°C, $Si_{10}Cl_{18}$ decomposes to substances of higher Si:Cl ratios. Above 800°C. a residue of silicon is obtained which is shown by X-ray studies to be amorphous.

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FLUORINE CONTAINING OXYHALIDES OF SULFUR

E. H. Grahn December 16, 1952

Introduction

In his work on fluorine containing oxyhalides of sulfur, Jonas (5) has described the preparation and properties of thionyl chlorofluoride, sulfuryl bromofluoride, and "thionyl tetrafluoride". Several compounds containing sulfur directly linked to fluorine and oxygen are known (7).

Name	Formula	Melting Point	Boiling Point
Thionyl fluoride	SOF_2	-110°C.	-43.8°C.
Sulfuryl fluoride	SO_2F_2	-120	-52
Sulfuryl chlorofluoride	SO_2ClF	-124.7	7.1
Thionyl chlorofluoride	$SOClF$	-139.5	12.3
Sulfuryl bromofluoride	SO_2BrF	- 86	40
"Thionyl tetrafluoride"	SOF_4	-107	-48.5

Thionyl fluoride

Thionyl fluoride, SOF_2, was first prepared by Meslans (6) in 1896 by reacting thionyl chloride with zinc fluoride. A better method, however, is that of Booth and Mericola (3), who obtained the compound by reacting thionyl chloride with antimony trifluoride using antimony pentachloride as a catalyst. Thionyl fluoride is a relatively stable compound which hydrolyzes only slowly in water and does not attack glass below 400°C. It is rapidly attacked by dilute alkali solutions.

Sulfuryl fluoride

Sulfuryl fluoride, SO_2F_2, was first described in 1901 by Moissan (8), who prepared it by the reaction of fluorine with sulfur dioxide in the presence of a platinum catalyst. It can be obtained in fair yields by decomposing barium fluosulfonate (9). Sulfuryl fluoride is a very stable compound, not being decomposed by hot water. It does not attack glass even at high temperatures, and molten sodium has no effect upon it.

Sulfuryl chlorofluoride

Sulfuryl chlorofluoride, SO_2ClF, was carefully characterized by Booth and Herrmann in 1936 (2). It was prepared in good yields from sulfuryl chloride and antimony trifluoride in the presence of antimony pentachloride as a catalyst. This compound is intermediate in stability and in reactivity between the chloride and the fluoride. It hydrolyzes slowly in water and very rapidly in dilute sodium hydroxide solutions. It does not attack dry glass, mercury, or the common metals at room temperature.

Thionyl chlorofluoride

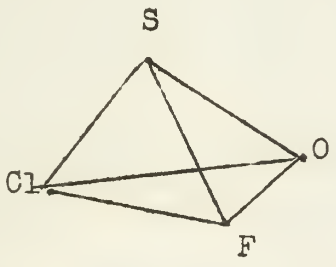
Thionyl chlorofluoride, SOClF, was prepared by Booth and Mericola (3) in 1940 by fluorinating thionyl chloride with antimony trifluoride using antimony pentachloride as a catalyst. Actually this is the same method used for the preparation of thionyl fluoride. On the fractional distillation of the reaction mixture, Booth and Mericola obtained approximately fifty percent thionyl fluoride, twenty percent thionyl chlorofluoride, five percent sulfur dioxide, and twenty-five percent unreacted thionyl chloride. Jonas (5) prepared it by reacting thionyl chloride (0.5 mol) with iodine pentafluoride (0.2 Mol) and then fractionally distilling the product. The following six fractions were obtained.

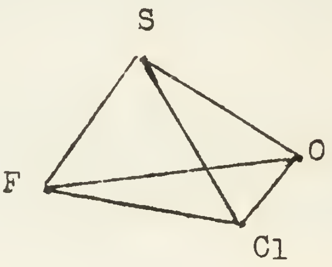
Fraction	Temperature Range	Products
1	-70°C. to -50°C.	SiF_4 and HCl
2	-50 to -36	HCl and SOF_2
3	-36 t0 -22	SOF_2 (12 cc.)
4	-22 t0 10	SOF_2 and SOClF
5	10 to 18	SOClF (10 cc.)
6	Rest	$SOCl_2$

Physical properties of thionyl chlorofluoride

Vapor density = 103.2 g./22.4 l. (calc. 102.5 g./22.4 l.)
The vapor pressure follows the equation, $\log p = 7.83 - \frac{1409}{T}$
The density may be expressed by the equation, $D=1.576-0.00224t$
Boiling point = 12.3°C.
Jonas was unable to determine a melting point for the compound. However, Booth recorded the melting point as -139°C.

Jonas hypothesized that thionyl chlorofluoride is actually a mixture of two stereoisomers, hence the abnormally low melting point as compared with thionyl chloride and thionyl fluoride. The following structures for thionyl chlorofluoride were suggested.





This is the only known inorganic thionyl compound with two different substituents. However, thionyl bromochloride was thought to have been prepared by Besson (1) from thionyl chloride and hydrogen bromide, but it was later proven by Hayes and Partington (4) to be an equimolecular mixture of thionyl chloride and thionyl bromide.

Thionyl chlorofluoride at 0°C. is a colorless volatile liquid. It reacts only very slightly with dry glass or quartz at room temperature. Under the catalytic effect of moisture, it forms silicon tetrafluoride, sulfur dioxide, and hydrogen chloride. It is hydrolyzed very quickly by water giving as products the fluoride ion, chloride ion, and sulfur dioxide or sulfite ion.

Sulfuryl bromofluoride

Jonas used two different methods for the preparation of this compound; the reaction of trichloromethanesulfuryl chloride with bromine trifluoride and secondly, that of reacting a mixture of bromine trifluoride, bromine, and sulfur dioxide. The first method gave a poor yield, since it appeared that the chief reaction was the formation of sulfuryl fluoride. The second method gave practically a quantitative yield.

Physical properties of sulfuryl bromofluoride

Vapor density = 162.0, 162.6 g./22.4 l. (calc. 163 g./22.4 l.

The vapor pressure follows the equation, $\log p = 8.03 - \frac{1610}{T}$

The density may be expressed by the equation, $D = 2.75 - 0.00298t$

The density of solid SO_2BrF at the temperature of liquid air is 3.16 g./cc.

Melting point = −86°±0.5°C.

Boiling point at atmospheric pressure = 40.0°C.

Sulfuryl bromofluoride is a colorless choking gas. At room temperature it reacts with dry glass, but not with quartz. With water in a sealed tube there is a vigorous reaction with the liberation of hydrogen bromide, hydrogen fluoride, and sulfuric acid. With a very small quantity of water, free bromine is liberated. The vapor of sulfuryl bromofluoride is fairly stable. It just begins to change color at a temperature of 320°C. and at 340°C. is completely decomposed into sulfur dioxide, sulfuryl fluoride, and bromine. There is also a reaction with quartz to form silicon tetrafluoride.

There was an attempt to prepare sulfuryl iodofluoride in a similar manner. Apparently the sulfur dioxide reacts with iodine pentafluoride alone, but not with a mixture of iodine pentafluoride and iodine. More clarification of this reaction is needed.

"Thionyl tetrafluoride"

This compound was prepared by passing a mixture of thionyl fluoride (18 g.) and fluorine over a platinum gauze at a temperature of 150°C. The product was distilled through a quartz fractionating column, and five fractions were collected.

Fraction	Temperature Range	Products
1	−90°C. to −64°C.	SiF_4 (small amount)
2	−64 to −52	SF_6 (4 cc.)
3	−52 to −49	SF_6, SO_2F_2, and SOF_4
4	−49 to −48	SO_4 (10 cc.)
5	Rest	SOF_2 (small amount)

Physical properties of "thionyl tetrafluoride"

Vapor density = 122.5 g./22.4 l. (calc. 123.9 g./22.4 l.)
The vapor pressure follows the equation, $\log p = 7.76 - \frac{1092}{T}$

The density may be expressed by the equation, $D = 1.653 - 0.00360t$
Melting point = −107° ± 0.5°C.
Boiling point (760 mm. Hg) = −48.5°C.

At room temperature "thionyl tetrafluoride" is a colorless pungent gas. It reacts violently with water and alkaline solutions, liberating sulfuryl fluoride and hydrogen fluoride. The sulfuryl fluoride slowly undergoes hydrolysis to give the fluoride ion and the sulfate ion. It reacts slowly at room temperature with mercury to give thionyl fluoride and mercurous fluoride.

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PREPARATION AND PROPERTIES OF URANYL CARBONATES

Richard A. Rowe December 16, 1952

Introduction

Discovery that minerals with the type formula $X^{+4}(UO_2)(CO_3)_3 \cdot n\,H_2O$ exist in nature (3) (where X = Na_2Ca, CaMg, Mg_2, and n = 6,12,18 respecitvely) prompted the French workers M. Bachelet, E. Cheylan, M. Douis, and J.C. Goulette (1,2) to study the formation of the alkali and alkaline earth uranyl carbonates. C. Guillemin (4) had prepared the magnesium compound and determined its physical constants. J. A. Hedvall (5) had previously prepared and described the monouranyltricarbonates of silver, mercury(I), mercury(II), copper(II), lead, cadmium, zinc, iron(II) cobalt and nickel.

Uranyl Carbonates of Sodium[1]

The only uranyl carbonate of sodium to have been prepared previously was $Na_4(UO_2)(CO_3)_3$, called sodium monuranyltricarbonate Bachelet and coworkers subsequently prepared $Na_6(UO_2)_2(CO_3)_5$ and $Na_6(UO_3)_3(UO_2)_2(CO_3)_3$. To simplify the nomenclature, these compounds will be designated as (A),(B), and (C) respectively.

By adding sodium carbonate to a solution of a uranyl salt, insoluble uranyl carbonate separates out.

$$(1)\ UO_2(NO_3)_2 + Na_2CO_3 \rightarrow UO_2CO_3 + 2NaNO_3$$
$$(2)\ UO_2CO_3 + 2Na_2CO_3 \rightarrow Na_4UO_2(CO_3)_3$$

The presence of sodium nitrate in the solution interfers with the separation of the uranyl carbonate. This disadvantage can be overcome by adding uranium (VI) oxide instead of the nitrate, but the formation of base somewhat limits the reaction.

$$(3)\ Na_2CO_3 + UO_3 + H_2O \rightarrow UO_2CO_3 + 2NaOH$$
$$(4)\ UO_2CO_3 + nNa_2CO_3 \rightarrow UO_2CO_3 \cdot n\ Na_2CO_3$$

The free NaOH formed in accordance with equation (3) will react with UO_3 to form sodium ~~nitrate~~. ~~carbonate~~ diuranate

$$(5)\ 2NaCH + 2UO_3 \rightarrow Na_2U_2O_7 + H_2O$$

The formation of (A) can therefore be represented as follows:

$$(6)\ 3Na_2CO_3 + 3UO_3 \rightarrow Na_4UO_2(CO_3)_3 + Na_2U_2O_7$$

The preparation of uranyl carbonates is best accomplished by interaction of uranium(VI)oxide with sodium bicarbonate since only uranyl carbonates remain in solution. By varying the quantities of the reagents it is possible to obtain not only compound (A) and also (B) and (C).

$$(7)\ UO_3 + 4NaHCO_3 \rightarrow \text{(A)}\ Na_4UO_2(CO_3)_3 + CO_2 + H_2O$$
$$(8)\ 2UO_3 + 6NaHCO_3 \rightarrow \text{(B)}\ Na_6(UO_2)_2(CO_3)_5 + CO_2 + 3H_2O$$
$$(9)\ 5UO_3 + 6NaHCO_3 \rightarrow \text{(C)}\ Na_6(UO_3)_3(UO_2)_2(CO_3)_5 + CO_2 + 3H_2O$$

The formation of compounds (B) and (C) is not to be considered as simple as is shown in equations (8) and (9), but rather as involving the stepwise addition of uranium(VI)oxide and carbon dioxide to compound (A).

$$(10)\ 3Na_4UO_2(CO_3)_3 + UO_3 + CO_2 \rightarrow 2Na_6(UO_2)_2(CO_3)_5$$
$$(11)\ Na_6(UO_2)_2(CO_3)_5 + 3UO_3 \rightarrow Na_6(UO_3)_3(UO_2)_2(CO_3)_5$$

Compounds (a), (B) and (C) have been prepared by mixing stoichiometric quantities of uranium(VI) oxide and sodium bicarbonate. At room temperature the rate of the reaction is very slow since the uranium(VI) oxide goes into solution slowly. The quickest method for obtaining compounds (A) and (B) is to dissolve, in the case of (A) a 1:4 mole ratio of $UO_3/NaHCO_3$ in a liter of water, and in the case of (B) a 1:3 mole ratio. After continuous agitation for two days the undissolved uranium(VI) oxide is filtered off. Within two days the filtrate will deposit a greenish precipitate. Precipitation will be accelerated by adding alcohol or acetone. Compound (C) can be obtained by starting with a solution of compound (B) and treating it with excess uranium(VI)oxide. Carbon dioxide is bubbled through the solution during the process. Compounds (A) and (B) dissolve slowly in water to give stable solutions at 20° which contain 204 g./l., and 190 g./l. respectively. Dilute sulfuric acid and (A) react with evolution of CO_2 gas.

$$(12)\ 3H_2SO_4 + Na_4UO_2(CO_3)_3 \rightarrow UO_2SO_4 + 2Na_2SO_4 + 3CO_2 + H_2O$$

Both (A) and (B) decompose to form insoluble uranyl compounds when the pH is brought into the range of 4 to 9.

Ammonia incompletely precipitates the uranium in the form of ammonium uranate. Addition of sodium hydroxide results in the precipitation of sodium uranate. Addition of sodium carbonate or bicarbonate to compound (B) brings about a conversion into compound (A).

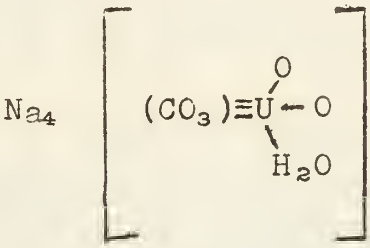
$$(13)\ Na_6(UO_2)_2(CO_3)_5 + 2NaHCO_3 \rightarrow 2Na_4UO_2(CO_3)_3 + CO_2 + H_2O$$

Complete precipitation of uranyl phosphate $UO_2(HPO_4)\cdot 4H_2O$ takes place in the presence of phosphate ion. When oxygen is passed through the solution of a uranyl carbonate uranium peroxide ($UO_4 \cdot 2H_2O$) is presumably formed. Thermal decomposition begins for each of the three compounds at the following temperatures: (A) 420°, (B) 410°, (C) 400°. These compounds can be regarded as the double salts - (A) $2Na_2CO_3 \cdot UO_2CO_3$, (B) $3Na_2CO_3 \cdot 2UO_2CO_3$, and (C) $3Na_2(CO_3) \cdot 2UO_2CO_3 \cdot 3UO_3$. Uranyl carbonate decomposes between 400-430° as follows:

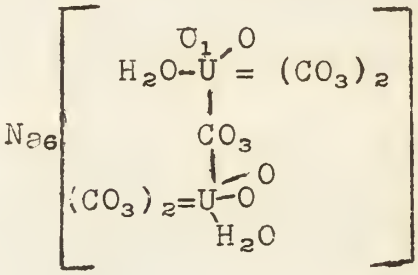
$$(14)\ UO_2CO_3 \rightarrow CO_2 + UO_3$$

Precipitation occurs when solutions of these compounds are heated. Dissolution of the resulting products is slow. It is therefore assumed the solution is accompanied by hydration and that this hydrated state is unstable and loses water when heated or when a dehydrating solvent is added. If a coordination number of 6 is assumed for the uranium VI, the following structures can be written for compounds (A) and (B) in solution (according to the authors).

(A)



(B)



The dehydration of the hydrated products as shown in the above structures leads to the formula for the precipitated products. The X-ray patterns of compounds (A) and (B) do not present qualitative differences.

Uranyl Carbonates of the Alkaline Earths[2]

Two methods have been employed to prepare the alkaline earth uranyl carbonates. Uranium(VI)oxide may be allowed to react with the alkaline earth bicarbonates. However, only the alkaline earth bicarbonates of magnesium, calcium, and strontium are soluble enough to make this method feasible. The alternative second method involves double decomposition between soluble salts of the alkaline earth metals and the corresponding sodium uranyl carbonate. Neither of these methods has given satisfactory results in the formation of uranyl carbonates of beryllium.

Uranyl Carbonates of Magnesium - Compound Mg(A) - $Mg_2UO_2(CO_3)_3$ was prepared by reacting the stoichiometric amounts of UO_3 and $MgH_2(CO_3)_2$ in water kept saturated by a stream of CO_2 gas.

$$(15)\ UO_3 + 2MgH_2(CO_3)_2 \rightarrow Mg(A) + CO_2 + H_2O$$

Mg(A) is a lemon yellow solid which is strongly hydrated, probably 18 molecules of water, and is very efflorescent in air. It dissolves into its water of crystallization at 60°. If a UO_3 and a solution of Mg(A) are agitated with CO_2 gas, an equilibrium mixture of compounds Mg(B) and Mg(C) is formed. After 48 hours of deposition, a product was collected which had a U/Mg ratio equal to 2.4.

Compound Mg(B) was obtained by reacting the proper amounts of Mg(A) with UO_2CO_3.

$$(16)\ 3Mg_2(UO_2)(CO_3)_3 + UO_2CO_3 \rightarrow 2Mg_3(UO_2)_2(CO_3)_5$$

Uranyl Carbonates of Calcium - Two methods of preparation can be used; The purest products are obtained by allowing the bicarbonate to react with uranium(VI)oxide. Compound Ca(A) can be obtained in a very pure state. It precipitates as a decahydrate in the form of greenish-yellow crystals, which are stable in air. It loses 8 molecules of H_2O at 90°, and it becomes completely anhydrous at 180°. Under ultraviolet light it emits a greenish luminescence. Compound (B) was prepared by allowing stoichiometric amounts of UO_3 and Ca(A) to react. It can also be made by the interaction of calcium nitrate with Na(B) as follows:

$$(17)\ 3Ca(NO_3)_2 + Na_6(UO_2)_2(CO_3)_5 \rightarrow Ca(B) + 6NaNO_3$$

If an excess of UO_3 is allowed to react with Ca(B) a precipitate is obtained which corresponds to neither compound Ca(B) nor Ca(C). As in the case of the magnesium salts, it is likely that an equilibrium mixture of these compounds exists in solution. The solubility of calcium uranyl carbonates increases with an increase in temperature. The solution becomes turbid at 60°, but the precipitate can be dissolved by passing carbon dioxide through the solution.

Uranyl Carbonates of Strontium - The best method for preparting Sr(A) is by the interaction of an excess of strontium chloride with Na(A).

$$(18)\ 2SrCl_2 + Na_4(UO_2)(CO_3)_3 \rightarrow Sr_2(UO_2)(CO_3)_3 + 4NaCl$$

The precipitate contains 9 molecules of water and exists in the form of small crystals which exhibit a green luminescence under ultraviolet light. Compound (B) cannot be prepared by either of the two general methods due to the extreme insolubility of Sr(A) which precipitates before Sr(B) can be formed.

Uranyl Carbonates of Barium - Interaction of Na(A) with barium chloride yields a greenish yellow precipitate corresponding to the 6 hydrate of Ba(A). The compound $Ba(B)\cdot 4H_2O$ can be obtained by a similar method. This compound is not fluorescent like Ba(A). Both compounds are insoluble and decompose in boiling water.

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THE NATURE OF IODINE SOLUTIONS

Ervin Colton January 6, 1953

Introduction

It is well known that iodine solutions are either violet or brown, the color depending upon the solvent (1). Such solvents as carbon disulfide, carbon tetrachloride, and saturated hydrocarbons form violet solutions with iodine, while brown solutions result with alcohols, ethers, ketones and organic nitrogen bases. Solvents yielding violet solutions are called "non-active" solvents, while those giving brown solutions are called "active" solvents. The case of iodine in benzene is somewhat anamolous, for the color of the resulting solution is red-violet which changes to violet when the solution is heated.

Precise molecular weight measurements have shown that iodine is present in the diatomic state in all solvents investigated thusfar (2). Hildebrand (3) has shown that the violet solutions form a series of "regular solutions", i.e., solutions which are formed from their components with the same change in entropy as occurs in the formation of an ideal solution of the same concentration. In these cases, the solubility of iodine may be represented by the family of curves

$$\log N_2 = 2.264 - [876.5 + k(1-N_2)^2]x1/T$$

where N_2 is the mole fraction of iodine in a solution saturated at the absolute temperature T, and k is a parameter, approximately independent of temperature for each solvent, whose value depends upon the energy of vaporization of the solvent. Approximate values of k for solutions of iodine in various solvents are shown below:

Solvent	CS_2	$CHCl_3$	$TiCl_4$	CCl_4	C_6H_{16}	$SiCl_4$
k	190	300	310	390	450	490

No such family of solubility curves can be used for iodine in brown solutions, thus indicating the probable formation of new molecular species.

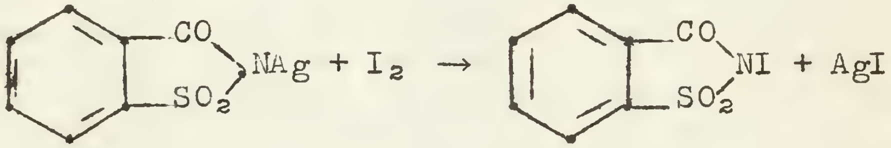
Spectrophotometric investigations show an absorption maximum in the region 515-525 mμ for iodine in "non-active" solvents.

Solvent	Max., mμ	Reference
Chloroform	520	(4)
Carbon tetrachloride	520	(4)
	517	(5)
	518	(6)
	520	(7)
	518	(8)
Carbon disulfide	520	(4)
	518	(5)
	518	(9)
n-Hexane	535	(10)

Iodine in brown solutions is much more reactive than the free element in the violet solutions. Physical measurements indicate that the brown solutions contain iodine chemically bound to the solvent, in equilibrium with free iodine. Each of the compounds forming brown solutions with iodine contains an element capable of acting as a donor in the formation of coordinate covalent bonds. Hildebrand and Glascock (11) studied the change in the freezing point of solutions of iodine in an "inactive" solvent brought about by the addition of a small amount of a third substance, itself either an "inactive" or "active" solvent. In those cases where the lowering was less than that calculated for the iodine on the basis of the dilute solution law, they concluded that there must be at least partial combination of iodine with the second solvent. Only with the "active" solvents was a large deviation observed.

$$I_2 + n(\text{"active" solvent}) \rightleftharpoons (\text{"active" solvent})_n \cdot I_2$$

Brown solutions of iodine in ether, alcohol, dioxane, among others, react with the silver derivative of saccharin to yield the theoretical quantity of silver iodide. Violet solutions only react slightly.



Iodine solutions of some completely fluorinated tertiary aliphatic amines as heptacosafluorotributylamine, $(C_4F_9)_3N$, pentadecafluorotriethylamine, $(C_2F_5)_3N$ and heptadecafluorodiethylpropylamine, $(C_2F_5)_2N(C_3F_7)$, are violet (12). Violet solutions are ordinarily observed for "non-active" solvents; in these amines the presence of three large alkyl groups and the numerous fluorine atoms appears to decrease tremendously the availability of the electron pair on the nitrogen atom and thus prevents the formation of a brown solution such as usually results with a nitrogen base.

Hildebrand and Benesi (5) have investigated, spectrophotometrically, the interaction of iodine with various substituted benzenes. In the visible region of the absorption peaks of these solutions showed moderate shifts toward shorter wave lengths. Each of the aromatic hydrocarbon solutions had an intense absorption band in the ultraviolet region, shown to be characteristic of a complex containing one I_2 and one aromatic hydrocarbon molecule.

Solvent	u.v. λ max., mμ	visible λ max., mμ
Benzene	297	500
Toluene	306	497
o-Xylene	319	497
p-Xylene	315	495
Mesitylene	333	490

Experimental Investigations

The exact nature of the binding between iodine and solvent in the brown solutions is still not well understood. The case of iodine in pyridine is an example. Audrieth and Birr (13) studied the change of conductivity of iodine in pyridine with time and explained their observations by assuming the presence of the following species in such solutions:

$$py + I_2 \rightleftharpoons Ipy^+ + I^- \rightleftharpoons py^{++} + 2I^-$$

$$2(py \cdot I_2) \rightleftharpoons Ipy^+ + I \cdot py \cdot I_2^-$$

A recent spectrophotometric investigation (14) seems to indicate that the broad band initially observed for a solution of iodine in pyridine gradually develops towards a maximum at approximately 373 mμ in 19 days. This peak is attributed to the triiodide ion.

The situation with iodine in quinoline is somewhat easier to study since the reaction between iodine and the amine is very rapid (12,14). Immediately after mixing, an initial maximum is observed at 370 mμ. A sharp increase in optical density, with no shift in the position of the maximum, is subsequently noted. This increase suggests that the maximum is due to a species resulting from reaction between the iodine and the quinoline. The maximum at 370 mμ is attributed to the triiodide ion. Proof of this is offered by the marked similarity of the absorption curves of iodine in quinoline to those of a known solution of triiodide in quinoline which also shows a maximum at 370 mμ. Even more conclusive proof that the maximum at 370 mμ is caused by the triiodide ion is offered by the rapid loss, up to 50%, of titratable iodine in solutions of iodine in quinoline. Upon standing, the strong absorption and maximum characteristic of the triiodide ion disappear; a new peak appears at 350-355 mμ. The latter maximum is attributed to an iodinated derivative that could not be isolated.

It is surprising to find that the relatively stable triiodide ion also reacts with quinoline, although at a much slower rate than does iodine. The triiodide maximum in solutions of tetra-*n*-butylammonium triiodide in quinoline gradually disappears. In solutions of iodine in quinoline in which, after 50% of the iodine has been consumed and the remainder presumably exists as triiodide ion, slow loss of titratable iodine still continues. It seems probable that the reaction proceeds *via* free iodine formation according to the equilibrium:

$$I_3^- + \text{quin} \rightleftharpoons I^- + \text{quin}\cdot I_2$$

Freshly prepared quinoline solutions of a series of substituted benzoates, e.g., *o*-, *m*-, and *p*-chlorobenzoates, *o*- and *m*-iodobenzoates, *m*- and *p*-nitrobenzoates, and *p*-bromobenzoate, of monoquinoline iodine(I), also show an absorption maximum in the region of 355 mμ. Rather rapid reaction involving removal of unipositive iodine, followed by formation of triiodide ion, is indicated by the initial decrease in optical density at 355 mμ and the subsequent rise in optical density with appearance of the maximum at 370 mμ. This latter peak disappears evantually and a third maximum is again observed at 355 mμ. This latter peak is due to the formation of an amorphous, violet, polymeric solid with an absorption peak at 355 mμ. These observations suggest a complex series of reactions in which the initial material undergoes decomposition with formation of iodine and polymeric products.

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SOME REACTIONS OF OZONE

Barbara H. Weil　　　　　　　　　　　　　　January 6, 1952

Van Marum in 1785 observed that oxygen subjected to an electric discharge had a peculiar odor and tarnished mercury. It was not until 1840, however, that Schönbein recognized that these properties were characteristic of a new gas which he named "ozone" from the Greek ozo, I smell. (1)

Ozone is more soluble than oxygen in water and more soluble in glacial acetic acid and chloroform than in water. It can be decomposed into oxygen by heat, by contact with powdered glass and, catalytically, with silver, platinum or manganese dioxide, lead dioxide and silver, cobalt and iron oxides. It is a powerful oxidizing agent, liberating iodine from a solution of potassium iodide. However, it has no action on potassium permanganate or chromic acid. Sulfur dioxide is oxidized to the trioxide and stannous chloride to stannic chloride in contact with ozone.

Ozone bleaches indigo solution and vegetable colors and converts moist sulfur, phosphorus and arsenic into their highest oxy-acids. It liberates halogens from their hydracids. Moist iodine is oxidized to iodic acid while dry iodine is converted into a yellow powder I_4O_9 with liberation of oxygen. (2,3)

For a long time it has been known that ozone reacts with the hydroxides of the alkali metals to produce peculiar, highly colored solids. (4) The reaction was first investigated extensively around 1900 by Baeyer and Villiger (5) who used the hydroxides of sodium, potassium, and rubidium for their investigations. They postulated the formation of "ozonates" of the formula M_2O_4. At about the same time, Bach (6) presented rather weak evidence for "ozonic acid", H_2O_4, formed in a manner analogous to the formation of H_2O_2 from Na_2O_2 and H_2SO_4. The potassium ozonate of Baeyer and Villiger was thus, he believed, the acid salt of ozonic acid, KO_4H. Evidence for the existence of ozonic acid has since been disproved, however. (9) Manchot and Kampschulte (7) found that the stability of the alkali metal ozonates, or ozonides, as they are now commonly named, increases with increasing atomic weight of the metal, the cesium derivative being the most stable and the lithium compound the least stable. They investigated the ozonides of the alkaline earths and found that here, too, stability increases with increasing atomic weight of the metal. The formation of all the ozonides is an exothermic reaction.

Traube, in a later work, postulated the product to be an addition compound of the metal hydroxide and oxygen, $(KOH)_2O_2$. (9)

Recently, the same reaction has been studied extensively by Kazarnovskii and co-workers for the purpose of elucidating the structure of the product. (10,11) They obtained, after reaction at low temperatures and extraction with ammonia, a product con-

taining 88-93% KO_3 with some KO_2, KOH and $KOH \cdot H_2O$. The mechanism $KOH + O_3 = KO_3 + OH$ is excluded by their thermodynamic data, so they postulate a possible mechanism involving the intermediate radical HO_2, namely, $KOH + O_3 = KOH \cdot O_3$; $KOH \cdot O_3 + O_3 \rightarrow KO_3 + O_2 + HO_2$. The decomposition in water proceeds according to: $KO_3 + H_2O = K^+ + OH^- + O_2 + OH$, followed by $2OH = H_2O + 1/2\ O_2$.

The free-radical nature of KO_3 was confirmed by these workers by magnetic measurements, molar susceptibility = $+1185 \times 10^{-6}$; hence, the magnetic moment = 1.67 Bohr magnetons, very close to the theoretical 1.73, corresponding to one unpaired electron. This confirms the formula KO_3 to the exclusion of K_2O_6 or $KOH \cdot O_3$. From results of molar electric conductivity, the compound can be formulated $K^+O_3^-$. The O_3- ion can be conceived as a resonance hybrid of $\bar{O}-O-O-$ and $-O-O-\bar{O}$ or the three-electron bond structures $O \overset{\cdots}{-} O-\bar{O}$ and $\bar{O}-O \overset{\cdots}{-} O$, with a third structure $\bar{O}-\dot{O}-\bar{O}$, the O-O bond being a hybrid between an ordinary and a three-electron bond. Preliminary X-ray deffractions studies reveal close similarity between the lattices of KO_3 and KN_3, tetragonal, of the K_2F_2 type.

Most recent work on the alkali metal ozonides has been done in this country by Whaley and Kleinberg who investigated the sodium, potassium and cesium derivatives.[12] They agreed with the Russians that assignment of the formulas NaO_3, KO_3 and CsO_3 to the colored, paramagnetic products is most consistent with the data obtained. However, chemical behavior of the product obtained from KOH, although mostly KO_3, would seem to indicate that the red solid is not a single chemical species. Analysis of the extracted cesium material even more strongly suggests the presence of another substance.

During the course of their investigations of the reactions of the alkali metal hydroxides and ozone, the Germans (5-9) had employed liquid ammonia as solvent and as a means for keeping the reactions cold. Manchot and Kampschulte (7) observed, further, that the bright orange color is observed even with pure, dry liquid ammonia by itself or such organic bases as methyl amine, dimethyl amine, piperidine, toluidine or aniline, but that was the extent of their investigations. Strecker and Thienemann, (13) thirteen years later, carefully investigated this reaction of ammonia and its derivatives. Experiments using pure, dry liquid ammonia and dry ozone showed that an unstable ozonide of ammonia is formed which on evaporation of excess ammonia is transformed to ammonium nitrate (98%) and nitrite (2%). Carius (14) and Ilosvay (15) had already carried out ozonization experiments with dilute aqueous ammonia solutions, the former obtaining NH_4NO_3, NH_4NO_2 and H_2O_2 as oxidation products; the latter could detect only nitrate and nitrite. Strecker and Thienemann found that ozone does not react nearly so completely with aqueous as with liquid ammonia.

With hydroxylamine, these workers found that hydroxylamine nitrate, which is rapidly formed, is the only product. Hydrazine hydrate yields essentially only nitrogen and water with small quantities of hydrazine nitrate and presumably ammonium nitrate. Hydrazoic acid is obtained in trace quantities. Tertiary amines such as trimethyl amine react violetnly, yielding exclusively the N-oxide.

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Papke, (16) studying relative rates of oxidation of ammonia in aqueous solution by ozone using as catalysts copper, cobalt and nickel salts obtained hydroxylamine as the first and rate determining step of the whole process.

In recent work on inorganic free radicals the decomposition of ozone in aqueous solutions catalyzed by OH^- has been studied by Weiss. (17) He showed that this can be accounted for by a chain reaction catalyzed by OH^- ion::

$$\begin{array}{ll} O_3 + OH^- \longrightarrow O_2^- + HO_2 & \text{initiating step} \\ \left.\begin{array}{l} O_3 + HO_2 \longrightarrow 2O_2 + OH \\ O_3 + OH \longrightarrow O_2 + HO_2 \end{array}\right\} & \text{chain propogation} \\ \left.\begin{array}{l} HO_2 + OH \longrightarrow O_2 + H_2O \\ HO_2 + HO_2 \longrightarrow O_2 + H_2O_2 \end{array}\right\} & \text{termination} \end{array}$$

Further, the reaction between ozone and hydrogen peroxide was explained quantitatively on this basis.

The most extensive work in the field of chain reactions of ozone in aqueous solutions has been done by Taube and Bray (18) and by Volman (19). The interaction of ozone and hydrogen peroxide in acidic aqueous solutions can be presented by two overall equations:

A. $O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$

B. $2O_3 \longrightarrow 3O_2$

The mechanism involves the following steps:

(1) $H_2O_2 + O_3 \xrightarrow{k_1} Oh + HO_2 + O_2$

(2) $HO_2 + O_3 \xrightarrow{k_2} OH + 2O_2$

(3) $OH + O_3 \xrightarrow{k_3} HO_2 + O_2$

(4) $OH + H_2O_2 \xrightarrow{k_4} HO_2 + H_2O$

Reaction (1) is the chain-initiating step. Reactions (2) and (4) are the chain-propogation steps for the overall reaction A and reactions (2) and (3) those for reaction B. Whether the reaction

$$HO_2 + H_2O_2 \longrightarrow OH + H_2O + O_2$$

occurs in the system will not only depende on the ozone/H_2O_2 ratic but also on the acidity, as it is likely to proceed via the O_2^- ion. In acid solutions, e.g., 0.2N, it cannot occur to a measurable extent in this system, the pK of HO_2 being 2. As the reaction $O_2^- + H_2O_2 \longrightarrow O_2 + OH^- + OH$ is likely to require an activation energy of ca. five kcal., it could be considerably suppressed in the presence of ozone even at a pH of 2.

A study was made by Taube and Bray of inhibition of this reaction. All organic substrates (such as alcohols) act as inhibitors. Organic acids occupy a special position. Chlorides and bromides inhibit but not fluoride, in agreement with thermodynamic data.

Some metals are found to be effective catalysts, the greatest effect being obtained when two conditions are fulfilled, (a) the cation is oxidized by ozone by a monovalent valency change and (b) the oxidized cation is reduced rapidly by H_2O_2. The net effect is then a larger stationary concentration of free radicals, thus leading to an increased rate of reaction. Colbaltous and cerous ions fulfill these conditions and Taube and Bray have shown that these cations induce the decomposition of ozone even in the absence of hydrogen peroxide. They found it difficult to explain the effect of Cu^{+2} as the existence of an oxidation state Cu^{+3} has not been established beyond doubt. Uri[20] expressed the opinion that the basic interpretation of the effect of Cu^{+2} ion might be similar in principle to its action as promoter in the catalytic decomposition of H_2O_2. Owing to a large $e^{\Delta S/R}$ factor, the reaction $Cu^{+2} + HO_2 \longrightarrow Cu^+ + H^+ + O_2$ (or the corresponding reaction with the O_2^- ion) is extremely fast and could occur in this system, being followed by the oxidation of Cu+ by ozone, accompanied in turn by the formation of OH radicals to act as chain carriers, i.e., $Cu^+(HOH) + O_3 \longrightarrow O_2 + Cu^{+2} + OH^- + OH$. The lack of inhibitory effect of choride ions in the presence of cupric ions is not surprising as it is in agreement with the considerably increased efficiency of cupric-chloro-complexes as catalysts for the decomposition of hydrogen peroxide.

Hill (21,23) recently studied the decomposition of ozone induced by cobaltous ion and postulated a mechanism involving formation of the $Co^{+3}OH^-$ ion-pair. He presented thermodynamic data to support this proposed mechanism.

Yeatts and Taube (22) indicate that the reaction between chloride ion and ozone in aqueous solution does not proceed through free-radical intermediates such as OH radicals and chlorine atoms, but reacts through the hypochlorite ion:

$$(a)\quad O_3 + Cl^- \longrightarrow O_2 + ClO^-$$

$$(b)\quad Cl^- + ClO^- + 2H^+ \xrightarrow[\text{determining}]{\text{not rate-}} Cl_2 + H_2O$$

Szabó, (24) on the other hand, proposes a six-step mechanism for the reaction whereby the intermediates are the free-radicals ClO and ClO_2.

It is evident that much work remains to be done in the field of ozone reactions since most workers do not yet agree on the nature of these reactions or, indeed, on the nature of the products obtained.

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HYDRAZINE BY ELECTROLYSIS IN LIQUID AMMONIA

Robert N. Hammer January 13, 1953

Introduction:

Because of the great increase in the large-scale use of hydrazine, considerable attention is being given to the improvement of methods of synthesis. For the manufacture of hydrazine, the low cost and availability of ammonia make it the logical starting material, in spite of the highly unfavorable thermodynamic character of the reaction:

$$2\ NH_3\ (liq) = N_2H_4\ (liq) + H_2\ (g);\ \Delta F = +41.0\ kcal\ mole\ -1.$$

In principle, this non-spontaneous reaction may be driven to completion by supplying low voltage electrical energy in an electrolytic process in liquid ammonia.

Theoretical considerations:

Just as the electrolysis of many aqueous solutions results in the formation of oxygen at the anode and hydrogen at the cathode, so in acidic or basic liquid ammonia solutions the anode and cathode products normally are nitrogen and hydrogen, as is indicated by the following electrode reactions:

In acidic solution (i.e., NH_4Cl)

Anode: $4\ NH_3 = \frac{1}{2}\ N_2 + 3\ NH_4^+ + 3\ e$ (a)

Cathode: $3\ NH_4^+ + 3\ e = \frac{3}{2}\ H_2 + 3\ NH_3$ (b)

In basic solution (i. e., KNH_2)

Anode: $3\ NH_2^- = \frac{1}{2}\ N_2 + 2\ NH_3 + 3\ e$ (c)

Cathode: $3\ NH_3 + 3\ e = \frac{3}{2}\ H_2 + 3\ NH_2^-$ (d)

Liquid ammonia and water have many similar properties, but some of the fundamental dissimilarities of these two solvents play an important role in electrochemical phenomena in liquid ammonia. One of these is the unusually low value of the standard free energy of formation of ammonia. The recent data compiled by Jolly (1) gives a value of -2.7 kcal mole^{-1} for $\Delta F_{f(298°K)}$, while the corresponding value of water (2) is -54.64 kcal mole^{-1} -- over twenty times greater. If the value of ΔF_f for ammonia is corrected to -50°C (a temperature at which many electrochemical investigations have been carried out), it is found that $\Delta F_{f(223°K)} = -6.0$ kcal mole^{-1}. This leads to an extremely low value for the reversible decomposition potential of an ammonia solution in which the electrolysis products are N_2 and H_2:

$$E_{d(223°K)} = \frac{-\Delta F}{n\mathcal{F}} = \frac{-6.0}{3 \times 23.1} = 0.087\ volt$$

In comparison, the reversible decomposition potential of water is about 1.18 volts, or almost fourteen times greater.

If the experimental decomposition potential of liquid ammonia were near this value, the possibility of hydrazine formation by an electrolytic process would be exceedingly unlikely. Fortunately, the measured decomposition potential of solutions in liquid ammonia shows that in actuality this property may be as large as several volts, even at low current densities, owing to the existence of a large nitrogen overvoltage (3).

Electrolysis of solutions of bases

Pleskov (4), in 1945, suggested that hydrazine as well as nitrogen should be formed at the anode in the electrolysis of basic liquid ammonia solutions. In 1950, Gessler and Pleskov published (3) the observation that hydrazine is formed at a current efficiency of 5 to 10 per cent during the electrolysis of a KNH_2 solution. Even though all attempts by other investigators to repeat this work have failed, there is reason to believe that such a reaction should be possible. As is indicated in equation (c), the primary anode reaction in the electrolysis of an amide solution in liquid ammonia appears to be the discharge of the NH_2^- ion and the formation of nitrogen. However, formation of hydrazine might occur through such a mechanism as the following:

$$NH_2^- = [NH_2^{\bullet}] + e \qquad (e)$$

$$2\,[NH_2^{\bullet}] = H_2N{-\!-}NH_2 \qquad (f)$$

for which the overall half-reaction would be

$$2\,NH_2^- = N_2H_4 + 2\,e \qquad (g)$$

Even the reaction of the $[NH_2^{\bullet}]$ radical with the solvent could lead to hydrazine formation:

$$[NH_2^{\bullet}] + NH_3 = H_2N{-\!-}NH_2 + 1/2\,H_2 \qquad (h)$$

Apparently no effort has been made to detect H_2 in the anode gas.

The combination of the anode half-reaction (g) with the cathode half-reaction (d) shows that KNH_2 is not consumed in the process inasmuch as amide ions which disappear from the anolyte are replaced by an equivalent amount formed at the cathode. The overall reaction, then, represents the direct electrochemical conversion of ammonia into hydrazine and hydrogen:

$$2\,NH_3 \xrightarrow{\text{electrolysis}} N_2H_4 + H_2$$

Since hydrazine does not undergo electron reduction in liquid ammonia (5), it would seem unnecessary to prevent mixing of

the anolyte and catholyte.

Electrolysis of solutions of acids

Another possible approach to the electrolytic synthesis of hydrazine in liquid ammonia involves the use of a solution of an acid such as NH_4Cl. Almost twenty years ago Howard and Browne reported (6) that very small amounts of a reducing agent, presumably hydrazine, are formed by the electrolysis of NH_4Cl in liquid ammonia between platinum or graphite electrodes. Again, efforts to repeat this work have failed. Consideration of the mechanism of such a reaction suggests that the formation of hydrazine in acidic solutions is less likely than in basic ones. The formation of nitrogen at the anode in an acidic solution, as is indicated in the equation:

$$4\ NH_3 = 1/2\ N_2 + 3\ NH_4^+ + 3\ e \qquad (i)$$

may be the primary anode process or it may be the result of secondary reactions between free halogens, or other products of the electrolysis, and the solvent. If the latter were the case, the possibility of hydrazine formation would be more promising. However, there is reason to believe that this does not occur. The anode overvoltage of nitrogen in acid solutions is practically uniform, regardless of the anions present in the solution, except in the case of NH_4I (3). This seems to indicate that the primary electrode process is the same in all cases and is probably the direct electrochemical oxidation of the ammonia molecule, inasmuch as the concentration of NH_2^- ions in acidic solutions must be exceedingly small. Furthermore, there has never been found in the products of electrolysis any free halogens, other than iodine, or any intermediate products of their interaction with the solvent, such as NH_2Cl, NCl_3, etc. In the case of electrolysis of NH_4I solutions, Gessler and Pleskov reported (3) that about 20 per cent of the current is consumed in the separation of iodine. This might be expected from a consideration of the data in Table I, where it may be seen that the differences between the normal potentials of the halogens and the potential of nitrogen separation considerably exceeds the 1.4 volt overvoltage (3) of nitrogen in all cases except for iodine in acid solution.

Table I. The difference of normal potentials of halogens and the potential of nitrogen separation in liquid ammonia (3)

	Solution	Cl_2	Br_2	I_2
$E_{N_2} - E_{X_2}$	Acid	2.03	1.90	1.45
$E_{N_2} - E_{X_2}$	Alkaline	3.39	3.19	2.81

Arc electrolysis:

Still another approach to the electrochemical formation of hydrazine in liquid ammonia involves arc electrolysis. Experiments by Ingraham (7) with 4000 volt direct current discharges between a platinum anode and a cathodic surface in liquid ammonia have shown that hydrazine is formed in yields up to 0.2 per cent, based on ammonia disappearance. The yield increases rapidly with increasing current density. Since the yields are in excess of those calculated by Faraday's laws for the simple discharge of the amide ion, Ingraham suggested that hydrazine is probably produced by a chain reaction operating in the gaseous discharge above the liquid surface.

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NAPHTHAZARIN COMPLEXES OF THORIUM AND RARE EARTH METAL IONS.

Melvin Tecotzky Thesis Report January 20, 1953

Solutions of thorium salts show no absorption in the range 2000 - 10,000 A°, thus thorium cannot be identified by direct absorption spectra measurements(3). In general, there is a lack of color reactions for thorium. Formanek (1) has shown that when the dye alkannin is added to thorium salt solutions, one obtains a violet solution showing maximum absorption in the range 6055-6084A°.

Recently, in seeking a more satisfactory method for the determination of beryllium, Underwood and Neuman (5) developed a method first using alkannin and then an equivilant procedure using naphthazarin. Since alkannin is a substituted naphthazarin, the two compounds would be expected to behave similarly. These recent investigations of the naphthazarin complexes of beryllium have indicated that a study of the reactions of other metal ions with this reagent might prove fruitful. Inasmuch as alkannin and thorium had been shown to give a color reaction, it seemed logical to investigate the thorium naphthazarin system from this point of view.

THE REAGENT

Naphthazarin is prepared by the Friedel-Crafts Reaction of hydroquinone and maleic anhydride (4). The product is recrystallized from high boiling petroleum ether and is obtained as brown needles. Naphthazarin has the structure shown in Figure A.

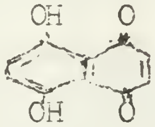

Fig. A

When dissolved in an organic solvent such as dioxane or ethanol, naphthazarin produces a red solution. Upon the addition of various metal ions the color of the solution changes, the color change being from red to reddish-blue or violet. Absolute ethanol has been used as a solvent for naphthazarin in this investigation. Metal ions have been used as aqueous solutions of their nitrate or chloride salts.

Upon the addition of a solution of thorium nitrate to a naphthazarin solution, there is a distinct color change from red to violet or purple, due to the formation of a thorium-naphthazarin complex. Solutions containing as little as 1×10^{-3} mg of thorium ion per ml. give visible evidence of complex formation. The color produced by rare earth ions with naphthazarin is a deeper red than the naphthazarin alone. The color change produced by rare earth ions is no where near as pronounced as the color change produced by thorium ion.

THORIUM-NAPHTMAZARIN COMPLEX ABSORPTION SPECTRA

The absorption spectrum of naphthazarin in ethanol is characterized by twin peaks at 4875 Å and 5166 Å and an inflection point at 5500 Å. The spectrum of the thorium-naphthazarin complex is also characterized by two peaks. The first appears at 5700 Å and the second appears at 6185 Å. This spectrum also has a point of inflection at 5375 Å. The spectrum of the complex is sufficiently different from that of the uncomplexed reagent to permit a study of the complex.

To determine the number of complex species present in solution, solutions of the thorium-naphthazarin complex were prepared in different mole ratios. Using the Cary Recording Spectrophotometer, it was observed that the curves obtained for all the solutions coincided quite well, thus indicating that only one colored complex species was present in solution.

THE MOLAR RATIO OF THE COMPLEX

An attempt to elucidate the empirical formula of the thorium-naphthazarin complex was made through the use of the method of Continuous Variations (2,6). Use was made of the difference in optical density between a naphthazarin solution and a solution of the complex of the same molarity. This difference in optical density, known as Y, between the complexed and uncomplexed reagent was plotted against concentration. The molar ratio where Y is a maximum is the molar ratio of the complex.

Similar results were obtained using the Cary Recording Spectrophotometer and the Beckman Spectrophotometer. When the values obtained were plotted, the maximum appeared at 34 mole % thorium and 66 mole % naphthazarin. This indicates a two to one complex, two naphthazarin molecules to one thorium atom.

Further evidence for a two to one naphthazarin-thorium complex was obtained by the application of the Molar Ratio Method. It has been reported by Yoe and Jones (7) that for a very stable complex, a plot of optical density against molar ratio of component B to component A, with A constant, rises from the origin as a straight line and breaks sharply to constant optical density at the molar ratio of the components in the complex. In every case the curve broke at a ratio of two moles of naphthazarin to one mole of thorium. This indicates a two to one complex and agrees with the data obtained from the method of Continuous Variations.

STABILITY OF THE COMPLEX

A stability study of the thorium-naphthazarin complex over a period of forty-three days indicated a very small change in optical density over this period of time. The complex appears to be stable enough in solution to work with for normal intervals of time without appreciable decomposition. When the complex was exposed to the direct rays of the sun, a much more rapid decomposition was found to take place. The spectrum of the complex was shifted to shorter wave lengths, and there was a considerable decrease in optical density.

LAKE LIKE CHARACTERISTICS OF THE COMPLEX

Upon the addition of ammonium hydroxide to a violet thorium-naphthazarin solution, containing excess thorium, a precipitate of thorium hydroxide forms. Upon agitation the solution becomes colorless and the precipitate becomes violet in color. If an excess of naphthazarin is present, the precipitate forms and the resulting solution is blue in color. Naphthazarin is blue in a basic solution. The thorium-naphthazarin material becomes adsorbed on the thorium hydroxide precipitate, in a manner similar to the adsorption of aluminon reagent on an aluminum hydroxide precipitate. The colloidal properties of the thorium-naphthazarin material have been shown through dialysis and flocculation of the material by strong electrolytes.

ADHERENCE TO BEER'S LAW

Various studies of the adherence of Beer's Law of solutions of the thorium-naphthazarin complex have been made. When the solutions prepared contained less than a two to one ratio of naphthazarin to thorium, no adherence to Beer's Law was found to exist. When, however, the ratio of naphthazarin to thorium was two to one or greater, the solution of the complex was found to adhere to Beer's Law in the range 10^{-5}M/1. This adherence to Beer's Law is important since it may provide a method for the quantitative determination of thorium.

RARE EARTH NAPHTHAZARIN COMPLEX ABSORPTION SPECTRA

The absorption spectra of solutions of lanthanum, praseodymium, neodymium, samarium, gadolinium, erbium, and yttrium ions combined with naphthazarin were examined with the Cary Recording Spectrophotometer. The spectra obtained were all similar in nature. The rare earth-naphthazarin spectra does not have as pronounced a characteristic peak as the thorium-naphthazarin complex does. The characteristic peak for the rare earth-naphthazarin complex is located between 6000 and 6050 Å. This is over 100 Å from the thorium-naphthazarin peak. This fact may well make it possible to determine thorium in the presence of rare earths through the use of naphthazarin.

The rare earth naphthazarin complexes exhibit the same properties as the thorium-naphthazarin complex; such as one complex species, a two to one ratio of naphthazarin to rare earth ion, adherence to Beer's Law and lake like characteristics.

An attempt has been made to evaluate the stability constants of the complexes formed. The determination of thorium in the presence of rare earths is being attempted at the present time.

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THESIS REPORT

Perry Kippur

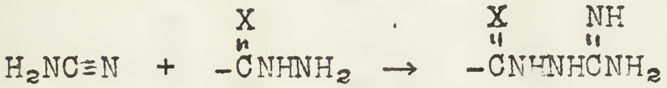
January 20, 1953

INTRODUCTION

The potential use of hydrazine as a specialty fuel and the commercial exploitation of certain hydrazine derivatives as a result of their biological activity has recently increased the amount of research activity in this field. These efforts have been directed towards the development of new procedures for both the preparation of hydrazine and the synthesis of hydrazine derivatives that may be employed as pharmaceuticals and agricultural chemicals.

The purpose of this investigation has been first, to develop a practical method for the preparation of thiocarbohydrazide, a compound which exhibits insecticidal, herbicidal, fungistatic and growth regulating properties and secondly, to condense cyanamide with certain hydrazides in order to extend further the general type reaction involving the addition of hydrazine, N-substituted hydrazines and hydrazides across the triple bond of the cyano group.

(1)



$$H_2NC\equiv N + -\overset{X}{\overset{\|}{C}}NHNH_2 \rightarrow -\overset{X}{\overset{\|}{C}}NHNH\overset{NH}{\overset{\|}{C}}NH_2$$

(where X = O,S, or NH)

I. THIOCARBOHYDRAZIDE

Historical

Thiocarbohydrazide has been prepared by the elimination of hydrogen sulfide from hydrazinium dithiocarbazinate (1) and the hydrazinolysis of S-methyldithiocarbazinate (2), diethyl xanthate (3) and thiophosgene. (1)(4)

The amphoteric character of thiocarbohydrazide is evidenced by its solubility in acids and bases and the formation of metallic and acid salts in suitable solvents. Thiocarbohydrazide enters into the reactions typical of the hydrazide group 1) reduction of silver ion, 2) solvation of compounds containing the cyano group (HOCN, HSCN) to produce normal or substituted N-carbamyl or N-thiocarbamyl derivatives, 3) solvolysis of acyl halides to yield N-acyl derivatives and 4) solvolysis of carbonyl compounds to yield the corresponding thiocarbohydrazones. Although alkylation of thiocarbohydrazide results in the formation of S-substituted derivatives, N-alkyl and N-aryl derivatives may be prepared by the reaction of certain thio compounds (CS_2, $CSCl_2$) with substituted hydrazines. The 1,5-di-alkyl and/or aryl thiocarbohydrazides may be oxidized to "thiocarbazones" (RN=NC (S) NHNHR) which are useful in the quantitative, colorimetric determination of metallic ions.

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Experimental and Discussion

The solubility of thiocarbohydrazide in water, ethanol, chloroform, carbon tetrachloride and hydrazine hydrate has been measured quantitatively; appreciable solubility is found only in the case of hydrazine hydrate. Thiocarbohydrazide is non-hygroscopic up to and including a relative humidity of 90%. It undergoes gradual thermal decomposition at 110°C. The pH of a saturated solution at room temperature is 6.95. From an x-ray diffraction pattern of thiocarbohydrazide, the d-spacings have been calculated.

A practical method for the preparation of thiocarbohydrazide by the direct reaction of carbon disulfide and excess aqueous hydrazine has been developed in which a yield of about 60% is obtained. The procedure requires the use of approximately a 5:1 mole ratio of hydrazine:carbon disulfide. For the quantities of starting materials employed (0.2 mole CS_2) in this investigation, it was found that a reflux time of from 1/2 to 1 1/2 hours is desirable. Acidification of the reaction mixture results in the decomposition of hydrazinium dithiocarbazinate which is formed by the initial combination of hydrazine and carbon disulfide. The use of dilute aqueous solutions results in a reduction of the yield of thiocarbohydrazide. The employment of an alcoholic solvent offers no advantage over the use of an aqueous solution. Additional quantities of thiocarbohydrazide (as much as 15%) are obtained by refluxing the mother liquor, subsequent to removal of the product from the initial reaction mixture. If the reaction is carried out on a larger scale (using molar quantities of CS_2 rather than 0.2 mole), an increase in the yield of several percent is obtained.

This new procedure possesses several advantages over previously reported methods: 1) better overall yields (60%) are obtained, 2) commercially available raw materials are employed (other methods require the preparation of special starting materials) and 3) the starting materials are not as difficult to handle as in the preparation of thiocarbohydrazide by the hydrazinolysis of thiophosgene. (1)(4) The new procedure is believed to be adaptable to a semi-continuous and/or continuous operation.

A mechanism for the elimination of hydrogen sulfide from hydrazinium dithiocarbazinate to give thiocarbohydrazide has been proposed. This mechanism involves the formation of an intermediate dithiocarbazinate ion which could then react with hydrazine prior to the elimination of hydrogen sulfide. Credence is lent to this mechanism as the excess hydrazine, which is required to give good yields of thiocarbohydrazide, favors each step of the postulated mechanism.

II. ADDITION OF CYANAMIDE TO HYDRAZIDES

Historical

The addition of cyanamide to hydrazides (equation 1) is similar to the condensations of cyanate and thiocyanate with hydrazides. Certain analogies exist, namely, first, the reagents attach themselves to the β-nitrogen atom of the hydrazide group, secondly, the

proposed mechanisms involve either rearrangement of an intermediate salt or molecular addition of the hydrazide across the carbon-nitrogen triple bond and thirdly, the condensations are pH dependent as a result of the stability of the reagents and/or products. It is more probable that cyanamide addition occurs according to the proposed molecular addition mechanism as the existence of a cyanamide salt in aqueous solution is improbable as a result of the weakly acidic character of cyanamide. Furthermore, cyanate and thiocyanate are relatively stable in alkaline solution as compared to cyanamide which readily undergoes polymerization to dicyandiamide under these conditions.

The procedures employed to affect cyanamide addition to hydrazides entail: 1) the use of an aqueous solution of cyanamide, 2) the employment of acidic aqueous solutions of sodium or calcium cyanamide, 3) the decomposition of nitrosoguanidine in aqueous solution and 4) the hydrazinolysis of S-alkylisothiouronium salts.

Although there are numerous reports in the literature concerning the addition of cyanamide to amines to produce guanidines, the preparation of aminoguanidine and its N-substituted derivatives represents one of the two instances of direct cyanamide condensation with hydrazine and substituted hydrazines. The preparation of bisguanylhydrazine dinitrate has also been described. (5)

Experimental and Discussion

The addition of cyanamide to semicarbazide, thiosemicarbazide, aminoguanidine and carbohydrazide has resulted in the preparation of the expected N-guanyl derivatives. These compounds have been characterized by conversion to the corresponding picrates and/or picrolonates. The new compounds which have been prepared include:

1) N-carbamyl-N'-guanylhydrazine hydrochloride
2) N-thiocarbamyl-N'-guanylhydrazine hydrochloride
3) Bisguanylhydrazine dihydrochloride
4) Guanylcarbohydrazide dihydrochloride

III. BIOLOGICAL ACTIVITY OF THE HYDRAZINE DERIVATIVES OF THE CARBONIC; THIOCARBONIC AND AMMONOCARBONIC ACIDS

A number of hydrazine derivatives have been evaluated for their antituberculin activity and also for their effect upon the blood pressure of hypertensive animals; however, none of the materials, which have thus far been tested, display any significant activity. The pharmacological evaluations have been carried out by personnel in the laboratories of the Eli Lilly Company.

Only a small number of hydrazine derivatives have thus far been evaluated for their insecticidal activity by the Department of Entomology at the University of Illinois. However, thiocarbohydrazide and 1-phenylthiocarbohydrazide have been found to be toxic to roaches.

A group of twenty-four hydrazine compounds consisting mainly of carbonic, thiocarbonic and ammonocarbonic acid derivatives have been subjected to an evaluation of their possible applications in the

agricultural chemical field. These tests have been carried out in cooperation with the Department of Agronomy at the University of Illinois.

Results have shown that methyl hydrazine sulfate, hydrazine sulfate and thiocarbohydrazide are effective as contact herbicides. Furthermore, methyl hydrazine sulfate, hydrazine sulfate, thiosemicarbazide, thiocarbohydrazide and 1-phenyl-thiocarbohydrazide show promise as fungicidal or fungistatic agents. A significant effect upon the growth of certain plants has been exhibited by thiocarbohydrazide, thiosemicarbazide and 5-aminotetrazole. A small number of hydrazine compounds display crop plant defoliant activity. An interesting observation which has been made during these biological tests is the production of albinism by bisthiocarbamylhydrazine, 5-amino-tetrazole and 1,2-diacetyl-3,5-diamino-1,2,3,5-tetrahydro-1,2,4-thiadiazole.

The results of these biological tests have repeatedly demonstrated that the presence of a thiohydrazide group $-C(S)N_2H_3$, enhances the biological activity of the compounds which have thus far been evaluated.

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Ion-Pair Formation in Acetic Acid

M. M. Jones   Feb. 24, 1953

In one of the earliest investigations on the properties of acetic acid as a solvent, Raoult (1) found that the freezing point depression of solutions of alkali acetates correspond to ideal behaviour. Later investigations by Raoult and Recoura (2) and Beckmann (3) confirmed and extended these observations. At that time workers in physical chemistry were chiefly concerned with what was considered to be anomalous behaviour of aqueous solutions of ionic compounds. The theory of Arrhenius had not yet been completely accepted; some of its glaring inadequacies were much discussed (4). At the same time some of its triumphs, such as the good agreement between the degree of dissociation determined by freezing point methods and conductivity studies (since shown to be fortuitous), seemed to indicate that the theory was in the main correct. The fact that the theory seemed incapable of giving a complete explanation for the properties of ionic solutions led to the development of two different schools of thought. The first took an almost purely thermodynamic viewpoint and found an able leader in G. N. Lewis. The second school of thought attempted to develop a solution on the basis of statistical mechanics. The first work of any consequence along the

latter line was attempted by S. R. Milner (5)-(8). The first widely successful treatment, by Debye and Huckel (9), offered several advantages over the earlier and somewhat similar work of Milner.

The theory of Debye and Huckel is familiar at least in a qualitative sense to most chemists. Less familiar are the attempts of others to overcome certain difficulties and approximations which are contained in the Debye-Huckel theory. One of these approximations was their solution of the Poisson-Boltzmann equation, relating the distribution of charge and the potential at a point in the solution. Soon after the appearance of the Debye-Huckel theory, Bjerrum devised a method which did not require a solution of this particular equation. This method of Bjerrum, and subsequent developments of it by other authors, has become known as the method of "ion-pairs" and is capable of furnishing a consistent picture of ionic solutions. It is most frequently applied to solutions in non-aqueous solvents of low dielectric constant although it is by no means limited to these.

Bjerrum assumed (10) that every ion within a miniumum distance of another ion of opposite charge is paired with that ion. Such an "ion-pair" acts as a single particle. By determining the probability of such ion-pairs, Bjerrum showed that such a theory could account for the activity coefficients of salts and the radii of ions in

dilute aqueous solutions. The methods outlined in this paper required tedious numerical work and were much less convenient in actual use than the simple formulae of Debye and Huckel.

Fuoss and Kraus (11) (12) later used this principle of Bjerrum's in the explanation of the properties of electrolytes in solvents of low dielectric constant. By combining the Ostwald dilution law with the ideas of Bjerrum, Fuoss and Kraus developed a method of estimating the degree of dissociation and the limiting equivalent conductance of these solutions. Extensive experiments by Kraus and coworkers have shown that the general pattern of behaviour of electrolytes in a large number of non-aqueous solvents is accurately predicted by this theory.

Although earlier studies in acetic acid attempted to use the principles outlined by Fuoss and Kraus, the first rigorous application of their theory to this solvent was made by Griswold (1943) in work which has not yet been published. Griswold collected very precise information on the effect of one salt on the solubility of another and also made a careful survey of the literature for similar data. In all cases the concept of ion-pairs was capable of explaining the effects quantitatively. Later Jones, under the direction of Griswold, provided an independent method of checking the assumption made by Griswold. In addition, these later studies provided

quantitative values for both dissociation constants and activity coefficients of the various solutes studied earlier by Griswold.

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IRON VERSENATES[1]

R. L. Rebertus March 3, 1953

The Iron(III) Complex

Chemical Properties.——The Iron(III) versenates, $NH_4FeY \cdot H_2O$ and HFeY, may be prepared according to the procedure of Brintzinger and coworkers[2]. A solution of the ion, FeY^-, is stable to acidified permanganate. Only partial reactions occur upon sulfide or thiocynate addition. No reaction takes place with o-phenanthroline, phthalate, or benzoate. Alkali hydroxides precipitate ferric hydroxide, and cupferron, $C_6H_5N \cdot NO \cdot ONH_4$, also precipitates the iron. Solutions of FeY^- are stable toward decomposition when stored in dark or red containers, but in sunlight the solution becomes colorless due to the reduction of the complex.

Physico-chemical Studies.——The titration of HFeY with sodium hydroxide reveals that it behaves as a strong acid. However, at high pH values a second inflection, accompanied by a color change, occurs due to the formation of the complex, $FeYOH^=$. This titration curve is compared with that of the weak dibasic acid, Na_2H_2Y, in Fig. 1.

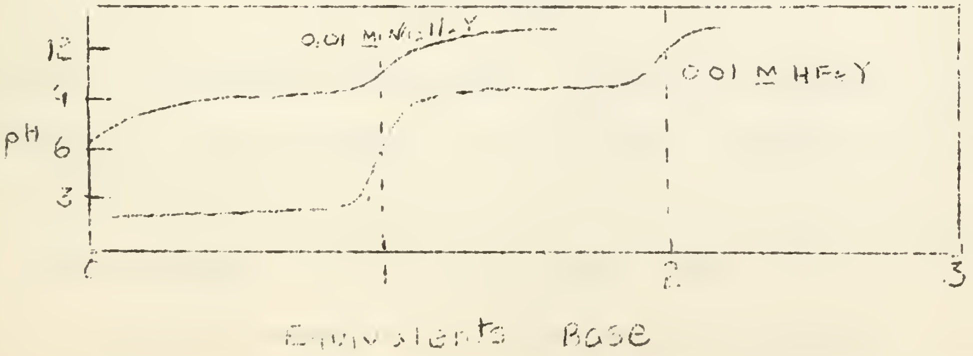

Fig.1.——Titration of HFeY and Na_2H_2Y with N_aOH.

The absorption of FeY^- at pH 2.5 is such that the solution appears yellow, but a pH 9.0 the orange color of $FeYOH^=$ appears. The method of Job[3] as modified by Vosburgh[4] was used to determine whether FeY^- is the only complex existing in acid solution. Two solutions of equal molarities, one of ferric ion and one of ethylenediaminetetraacetic acid, were mixed in differing ratios, and the optical densities of the solutions were measured at selected wave lengths. A plot of Z, the difference between the observed density and that calculated assuming no reaction, against x, a composition function, revealed only the 1:1 complex.

The dissociation constant of the ion, FeY^-, was determined by the radioactive indicator method. A solution containing 0.025 molar FeY^-, 0.60 molar H^+, and enough sodium perchlorate to give an ionic strength of 2.02 was held at 25° to allow equilibrium dissociation. Then equal volumes of this solution and of 0.025 molar $Fe^*(ClO_4)3$ were mixed. An instantaneous exchange of 15% was observed. This instantaneous exchange results from the mixing of the radioactive ferric ion with non-radioactive ferric ion from the equilibrium dissociation of the complex. This value is related to the fractional dissociation of the complex by

$$f = \frac{d(a + b)}{a + db}$$

where f is the fractional exchange, d is the fractional dissociation of the complex in the original equilibrated solution, and a and b are the total concentrations of added ferric ion and complex ion in solution after mixing. In this case a=b, and d calculates to be 0.081. Thus in the original solution the ferric ion concentration is 0.002 molar. In highly acid solution the predominating equation for the dissociation is

$$FeY^- + 4\,H^+ \rightleftharpoons Fe^{+++} + H_4Y$$

From this equation the following equilibrium expression can be used to calculate K_d:

$$\frac{(Fe^{+++})^2}{[(FeY^-)_0 - (Fe^{+++})]\,[(H^+)_0 - 4\,(Fe^{+++})]^4} = K_d/K_a$$

where K_d is the dissociation constant of FeY^-, K_a is the over-all dissociation constant for the acid, H_4Y, ($10^{-21.09}$), and the zero subscripts refer to total concentrations in the original solution before dissociation. The value of K_d is calculated to be 10^{-24}. Schwarzenbach and Heller[5] report a value of 10^{-25} from an e.m.f. study of the equilibrium constants.

Exchange between the complex FeY^- and $Fe^*(ClO_4)_3$ proceeds slowly, the half-time of exchange being several hours. A detailed investigation of the kinetics of exchange yielded the following rate law;

$$R = 0.47(FeY^-)(H^+)^3 + 0.015(FeY^-)(Fe^{+++}) + 0.14(FeY^-)(FeOH^{++})$$

In highly acid solutions the first term is the predominating one, whereas in more basic solutions the second and third terms contribute mostly to R.

Structure. —— The iron versenates are octahedral; each has optical isomers.

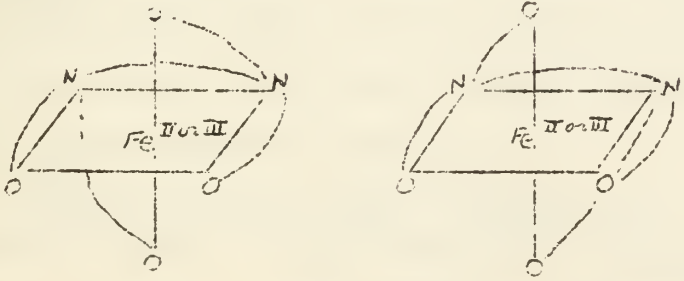

Fig. 2. - Possible Structures of Iron Versenates.

Commercial Application. —— Iron(III) versenate is commercially available. This complex has the ability to liberate iron at such a rate that it is easily assimilated by citrus trees, and it has been

The Iron(II) Complex

Chemical Properties.——No solid salts of this complex have been prepared. Oxygen in solution readily oxidizes this complex to FeY^-. Ammonium hydroxide (pH 9) does not decompose it, but alkali hydroxides give mixtures of ferric and ferrous hydroxides. The complex, $FeY^=$, is also decomposed by sulfide ion and o-phenanthroline. No reaction with ferricyanide ion occurs.

Physico-chemical Studies.——The acid, H_2FeY, behaves as a strong acid and only a single inflection in the tirration curve is noted. However, when the solutions are exposed to air, an inflection occurs after only one equivalent of base is added due to the formation of HFeY.

The spectrum of $FeY^=$ shows no absorption in the visible region.

The dissociation constant of the ferrous complex was determined by a procedure quite different from that used to determine the constant for the iron(III) complex. The iron(II) complex is of lower stability so that in solutions of intermediate acid concentration there is extensive dissociation with concomitant formation of weak acids from the $Y^{==}$ ion. A calculation of the dissociation constant is possible from a determination of the actual hydrogen ion concentration in a mixture of the complex and a known amount of acid and a knowledge of the acidity constants for ethylenediaminetetraacetic acid[6]. The following equations may be written.

$$(H^+)_o - (H^+) = (Y^{==})[4 \times 10^{21.09}(H^+)^4 + 3 \times 10^{19.09}(H^+)^3$$
$$+ 2 \times 10^{16.42}(H^+)^2 + 10^{10.26}\,H^+] + (HSO_4-)$$

$$(Y^{==}) = \frac{(H^+)o - (H^+) - (HSO_4)^-}{10^{21.69}(H^+)^4 + 10^{19.56}(H^+)^3 + 10^{16.72}(H^+)^2 + 10^{10.26}(H^+}$$

$$(Fe^{++}) = \sum_{x=0}^{4} H_xY^{x-4} = (Y^{==})[10^{21.09}(H^+)^4 + 10^{19.09}(H^+)^3 + 10^{16.42}$$
$$(H^+)^2 + 10^{10.26}(H^+) + 1]$$

$$(FeY^{=}) = (FeY^{=})_o - (Fe^{++})$$

In practice, sodium sulfate, sulfuric acid, and sodium ethylenediaminetetraacetato-ferrate(II) are coexistent in the solution, and the dissociation constant may be calculated from the above relations.

$$K_d = \frac{(Fe^{++})\ (Y^{==})}{(FeY^{=})} = 10^{-14}$$

The half-time of exchange between $FeY^{=}$ and Fe^{*++} is less than a minute. This is additional evidence for the lesser stability of the $FeY^{=}$ ion as compared to the FeY^{-} ion.

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Amphoterism in Non-aqueous Systems(1)

Harold J. Matsuguma March 3, 1953

I. Introduction:

Amphoterism has been studied very intensively in the field of aqueous solutions. The actual mechanism of the dissolution of hydroxide precipitates in excess base has long been a point of argument. Three concepts have been formulated.

The first, advanced by Hantzch(2), considers the process to be one of peptization. Solutions formed by such a process would be colloidal in nature, and indeed both true and colloidal solutions of chromium (III) hydroxide can be prepared under suitable conditions. Bredig, on the other hand, considered the amphoteric compound capable of acting either as an extremely weak acid or base. These two theories have been superceded by the third, developed by Pfeiffer(3). This latter theory and the one most widely supported at the present time explains the dissolution of amphoteric hydroxides as a coordination phenomenon in which the amphoteric element goes into solution usually as a soluble anionic hydroxo complex. Scholder and coworkers (4,5,6,7,8,9,10,11,12,13) have carried out an extensive series of investigations on the amphoteric behavior of several elements and their work confirms Pfeiffer's theory.

Recently amphoterism has been investigated in other ionizing, water-like solvents. It has been found that aluminum, zinc, tin, lead and chromium, all amphoteric in water, also possess this property in various other solvents.

II. Amphoterism in Specific Solvents:

The phenomenon of amphoterism has been noted in almost every non-aqueous solvent investigated. Many elements carry over amphoteric character from one solvent to another. In each case of amphoterism a coordination mechanism has been postulated to explain observations.

The Copper(II) ion(14,15) exhibits amphoteric character in liquid ammonia. Copper(II) nitrate dissolves in liquid ammonia to give a deep blue solution. When potassium amide is added an olive-green precipitate is formed; this precipitate dissolves upon addition of excess amide. Similar behavior is noted with the amides of the following elements; strontium(II), beryllium(II), zinc(II), silver(I), lead(II), aluminum(III) and gallium(III). Most, if not all, of these substances are initially only slightly soluble in liquid ammonia. but will dissolve when an excess of potassium amide is added. Some of the compounds which have actually been isolated as crystalline compounds are listed below:

Empirical Formula	Resolved Formula
$K_2[Ga(NH_2)_5]$	$Ga(NH_2)_3.2KNH_2$
$K_2[Zn(NH_2)_4]$	$Zn(NH_2)_2.2KNH_2$
$K_2[Na(NH_2)_3]$	$Na(NH_2)\ .2KNH_2$
$K[Sr(NH_2)_3]$	$Sr(NH_2)_2.KNH_2$

The cyanides of iron(III), silver(I) and mercury(II) possess amphoteric character in liquid hydrogen cyanide (14,16). All of these elements form insoluble cyanides in liquid hydrogen cyanide, but in every case these precipitates dissolve when an excess of the appropriate base analogue is added, e.g.;

$$FeCl_3 + 3[(C_2H_5)_3NH]CN \rightleftharpoons Fe(CN)_3\downarrow + 3[(C_2H_5)_3NH]Cl$$

$$Fe(CN)_3\downarrow + 3[(C_2H_5)_3NH]CN \rightleftharpoons [(C_2H_5)_3NH]_3[Fe(CN)_6]$$

Zinc(II) and copper(II) acetates are amphoteric in absolute acetic acid (14). Both elements precipitate as the acetates when sodium acetate is added to solutions of these elements. However, when an excess of the base is added the precipitates dissolve to form compounds which are analogous to the compounds formed in aqueous solutions when an excess of hydroxide is added to precipitates of the hydroxides.

$$ZnCl_2 + 2NaCH_3COO \rightleftharpoons Zn(CH_3COO)_2 + 2NaCl$$

$$Zn(CH_3COO)_2 + 2NaCH_3COO \rightleftharpoons Na_2[Zn(CH_3COO)_4]$$

In absolute nitric acid uranyl nitrate and cadmium(II) nitrate have been found to be amphoteric (17). Addition of an excess of tetramethylammonium nitrate to solutions of uranyl nitrate in absolute nitric acid gives the soluble tetramethylammonium trinitratodioxouranate(VI) complex.

$$UO_2(NO_3)_2 + [(CH_3)_4N]NO_3 \rightleftharpoons [(CH_3)_4N][UO_2(NO_3)_3]$$

Potassium nitrate, another base in absolute nitric acid, gives a complex compound when added to solutions of cadmium(II) nitrate in this solvent.

$$Cd(NO_3)_2 + xKNO_3 \rightleftharpoons Kx[Cd(NO_3)_{2+x}]$$

The actual composition of this compound has not yet been determined.

Aluminum(III) and tin(IV) sulfites and the oxides of bismuth(III), gallium(III) and antimony(III) and (V) have also been found to be amphoteric in liquid sulfur dioxide solvo(14,18). When bis-tetramethylammonium sulfite is added to a solution of aluminum(III) chloride in liquid sulfur dioxide, aluminum (III) sulfite precipitates. When an excess of the base is added the precipitate dissolves to give tris-tetramethylammonium trisulfitoaluminate(III). This compound reacts further with the acid, thionyl chloride, to give the insoluble sulfite once again.

$$2AlCl_3 + 3[(CH_3)_4N]_2SO_3 \rightleftharpoons Al_2(SO_3)_3\downarrow + 6[(CH_3)_4N]Cl$$

$$Al_2(SO_3)_3\downarrow + 3[(CH_3)_4N]_2SO_3 \rightleftharpoons 2[(CH_3)_4N]_3[Al(SO_3)_3]$$

$$2[(CH_3)_4N]_3[Al(SO_3)_3] + 3SOCl_2 \rightleftharpoons Al_2(SO_3)_3\downarrow + 6[(CH_3)_4N]Cl + 6SO_2$$

Tris-tetramethylammonium trisulfitoaluminate(III) is also formed when a solution of two moles of aluminum(III) chloride and seven moles of bis-tetramethylammonium sulfite in liquid sulfur dioxide is titrated with thionyl chloride.

Arsenic(III) sulfide in liquid hydrogen sulfide behaves analogously to aresenic(III) oxide in water(19). Arsenic (III) sulfide is only slightly soluble in this solvent, but when an excess of triethylammonium monohydrogen sulfide is added to the solution the soluble tris-triethylammonium trithioarsenate(III) complex is formed. The reaction is;

$$As_2S_3 + 6[(C_2H_5)_3NH](HS) \rightleftharpoons 2[(C_2H_5)_3NH]_3AsS_3 + 3H_2S$$

Aluminum(III) and chromium(III) are amphoteric in liquid hydrogen flouride(14). Addition of excess base to solutions of the fluorides of these elements usually results in the formation

of the hexaflouro complexes.

III. Summary:

Amphoterism has been found to exist in many non-aqueous solvents. In almost every case the reactions of amphoteric compounds in various solvents lead to the formation of complex compounds. Pfeiffer's theory, describing the process of dissolution of amphoteric hydroxides in aqueous solutions, has been found to be valid in the field of other ionizing, water-like solvents, whereas those due to Hantzch and Bredig cannot be successfully applied.

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Place in the Periodic System of the Heaviest Elements

Ervin Colton March 10, 1953

The heaviest elements refer to elements of atomic numbers 89-98, inclusive, i.e., actinium through californium. The suggested electronic configurations (beyond radon and xenon) for gaseous atoms of the actinide and lanthanide series are shown below for reference:

At. No.	Element	Configuration	At. No.	Element	Configuration
89	Ac	$6d^17s^2$	57	La	$5d^16s^2$
90	Th	$6d^27s^2$(or $5f^16d^17s^2$)	58	Ce	$4f^26s^2$
91	Pa	$5f^26d^17s^2$(or $5f^16d^27s^2$)	59	Pr	$4f^36s^2$
92	U	$5f^36d^17s^2$	60	Nd	$4f^46s^2$
93	Np	$5f^57s^2$(or $5f^46d^17s^2$)	61	Pm	$4f^56s^2$
94	Pu	$5f^67s^2$(or $5f^56d^17s^2$)	62	Sm	$4f^66s^2$
95	Am	$5f^77s^2$(or $5f^66d^17s^2$)	63	Eu	$4f^76s^2$
96	Cm	$5f^76d^17s^2$	64	Gd	$4f^75d^16s^2$
97	Bk	$5f^86d^17s^2$	65	Tb	$4f^96s^2$
98	Cf	$5f^96d^17s^2$	66	Dy	$4f^{10}6s^2$

Arguments according to Seaborg (1,2):

Present evidence points to the conclusion that it is the 5f electron shell that is being filled in these heaviest elements. Further, the evidence seems to suggest a second rare-earth like series, beginning with actinium in the same sense that the "lanthanide" series begins with lanthanum. Such an "actinide"series is suggested on the basis of the following observations: (A) chemical properties, (B) absorption spectra in aqueous solution and crystals

(C) crystallographic structure data, (D) magnetic susceptibility and (E) spectroscopic data.

A. Chemical properties: A table of oxidation states of the lanthanide and actinide elements is shown below. Values in parentheses have been reported but are unstable:

atomic no.	89	90	91	92	93	94	95	96	97	98
element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
oxid. state		(+2)					(+2)			
	+3	(+3)	(+3)	+3	+3	+3	+3	+3	+3	+3
		+4	+4	+4	+4	+4	+4		+4	
			+5	+5	+5	+5	+5			
				+6	+6	+6	+6			

atomic no.	57	58	59	60	61	62	63	64	65	66
element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
oxid. state						+2	+2			
	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
		+4	+4						+4	

The regularity of the +3 state in the lanthanide series is not so well pronounced in the actinide series. The +4 oxidation state, as well as the +3 state, seems to characterize the actanides. It becomes increasingly difficult to effect oxidation to higher valence states with increasing atomic number among heavier elements. The following table shows some oxidation potentials of the actinides in 1M aqueous solution:

element	III to IV	IV to VI
U	+0.63 v.	-0.60 v.
Np	-0.14	-0.94
Pu	-0.95	-1.11
Am	~ -2.6	

The metals of the elements Th to Am bear striking resemblance to those of the rare earth metals. A marked similarity is also noted in that americium ($5f^7 7s^2$) and europium ($4f^7 6s^2$) both have densities much lower than those of their neighbors.

B. Absorption spectra in aqueous solution and crystals:

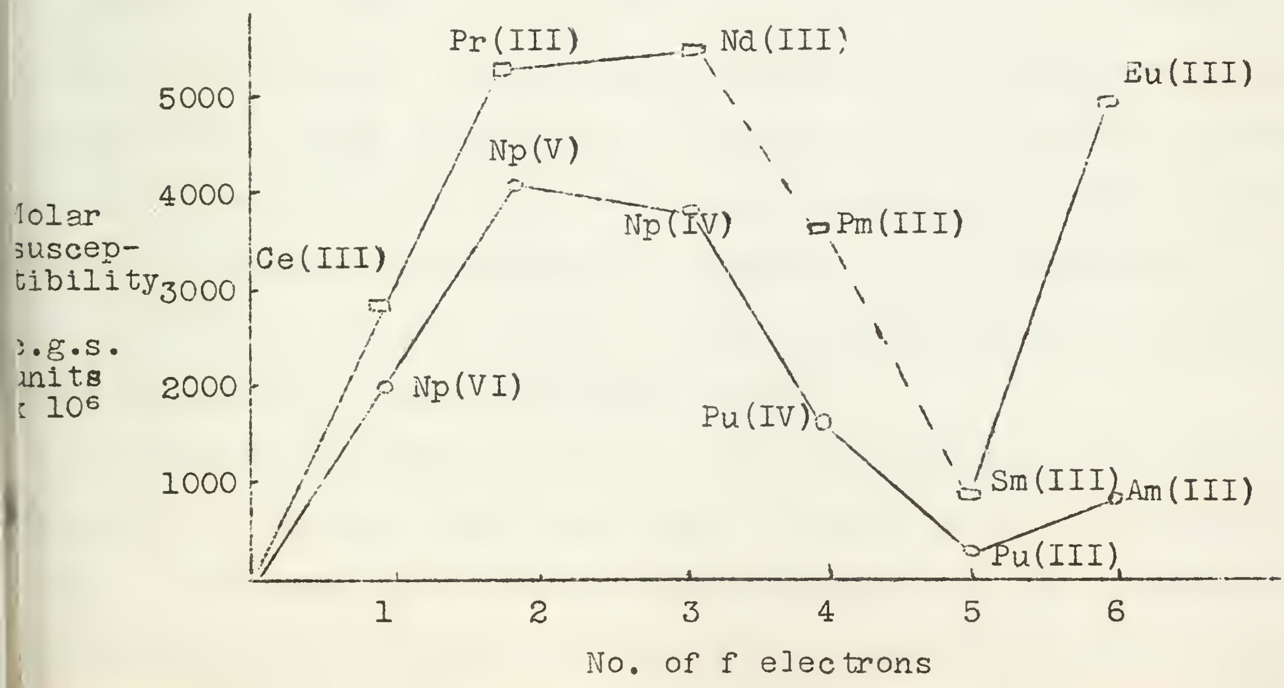
Sharp absorption bands, to a large degree in the visible region, are characteristic of the lanthanide series - a series whose properties are ascribed largely to the 4f electrons. The absorption spectra of aqueous tripositive actinide elements are strikingly similar to the spectra of the tripositive lanthanide elements; thus lending support to the concept that 5f electrons are involved in the building up of the actinide group. It has also been observed that the absorption spectra become greatly simplified as the middle of each of the two series is approached. The spectra for gadolinium and curium, each with seven f electrons, show only one sharp peak between 2000 and 11,000 A^{o}, whereas for the other elements of both series the spectra are more complex. Absorption spectra with crystals, especially those of americium halides, reveal sharp lines with widths comparable to the sharpest rare earth spectra.

C. Crystallographic structure data: Zachariasen has observed the isomorphism of the compounds ThO_2, PaO_2, UO_2, NpO_2, PuO_2 and AmO_2, and a regular decrease in radius of the metallic ion in these oxides. He has also used x-ray diffraction studies to determine the structure of a large number of compounds of Th, U, and the transuranium elements. The fluorides ThF_4, UF_4, NpF_4 and PuF_4 are of identical structure types as are the chlorides UCl_3, $NpCl_3$, $PuCl_3$ and $AmCl_3$. Calculations of ionic radii show a progressive decrease in size with increasing atomic number, analogous to the well-known lanthanide contraction. The compounds of the rare-earth elements are in turn isomorphous with the corresponding compounds of the actinide elements. The following table illustrates these considerations:

Ionic radii of actinide and lanthanide elements

No. of 4f or 5f elns.	Actinide series				Lanthanide series	
	III state		IV state			
0	Ac^{+3}	1.11 A°	Th^{+4}	0.95 A°	La^{+3}	1.04 A°
1	(Th^{+3})	(1.08)	Pa^{+4}	0.91	Ce^{+3}	1.02
2	(Pa^{+3})	(1.06)	U^{+4}	0.89	Pr^{+3}	1.00
3	U^{+3}	1.04	Np^{+4}	0.88	Nd^{+3}	0.99
4	Np^{+3}	1.02	Pu^{+4}	0.86	Pm^{+3}	(0.98)
5	Pu^{+3}	1.01	Am^{+4}	0.85	Sm^{+3}	0.97
6	Am^{+3}	1.00			Eu^{+3}	0.97

D. Magnetic susceptibility: One would expect magnetic measurements on compounds of the heaviest elements to give information on the quantum states of the responsible electrons. However, the situation is complex and the exact behavior of the heaviest elements on the basis of either 5f or 6d electrons has not yet been worked out. Yet, qualitatively speaking, observed paramagnetic behaviors of a number of ions in various oxidation states are similar to those of the lanthanide group. The following figure brings out these qualitative similarities:



E. Spectroscopic data: Information in this field is still rather scarc as far as the heaviest elements are concerned. Investigation of the spectrum of uranium atoms gave the lowest state of neutral uranium as $5f^3 6d^1 7s^2$, a consistent configuration since uranium is the third elemen in the series. Observations on gaseous Th^+ indicate that the 5f and 6d electrons are very close in the neutral, free thorium. Qualitative comparisons of the emission spectra of americium and europium show a strong analogy between the intensity of the lines, thus suggesting strongly that the configuration for gaseous Am in the ground state should be $5f^7 7s^2$.

Arguments against the "actinide" series (3,4,5):

On the basis of observations that the heavier elements exhibit both +3 and +4 oxidation states, Zachariasen prefers to speak of a "thoride" series for the tetravalent states and of an "actinide" serie for the trivalent states.

Thorium has been shown to be a true homologue of zirconium and hafnium. The great instability in aqueous solution of the triidides of thorium, zirconium and hafnium is in marked contrast to the stabili of cerium triiodide. Protactinium is similarly a homologue of niobium and tantalum. Ease of oxidation of uranium to the +6 state brings out its strong resemblance to tungsten and emphasizes its lack of similarity to neodymium. Uranium is most stable in the +6 state; if it were to be regarded as an "actinide", similar to the lanthanides, it should exist primarily in the +3 oxidation state.

Seaborg's arguments leading to the designation of the series as the actinide series, insofar as they are based on direct chemical evidence, would involve an extrapolation backward from the proposed $5f^6$ configuration for americium +3 and $5f^7$ for curium +3. Some of the di

crepancies between chemical properties and electronic structure come about because of the slight difference in energy between the 5f and 6d levels. Coryell (5) suggests that these discrepancies may be resolved by recognition of a delay in the filling of the 5f subshell.

Conclusion: On the basis of the present evidence, both chemical and electronic, and the opinions of various qualified workers, the views of Coryell seem to be more rational. The heavier elements constitute a "uranide" series rather than an "actinide" series. The periodic classification, in part, would appear thusly:

La				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
	Hf	Ta	W									
	Th	Pa	U				Np	Pu	Am	Cm	Bk	Cf
Ac												

Note: As a tool in remembering the elements in the two series, the following mnemonics may prove useful:

Lancer prince needs 61 small European gods to be dyed wholly early tomorrow. Why be ludicrous?

Actual thoughts pass under Neptune's public amnesty, calming balky coffles.

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Complex Anion Determination by Ion Exchange

M. K. Snyder

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While measuring the potential of cadmium amalgam electrodes, Leden (3) found evidence for the formation of an anionic cadmium sulfate complex. Fronaeus (2) calculated that the copper in a 0.01 M copper sulfate solution made 0.5 M with respect to sodium sulfate is present as an anionic complex, to the extent of eighty per cent. In order to clarify this situation, Leden (4) studied these complexes with ion exchangers.

For the study, Amberlite IRA 400 was used. In the first experiments, solutions of cadmium perchlorate, sulfate, chloride, and iodide were put through a column containing the resin in the perchlorate, sulfate, chloride or iodide form. Then the resin was washed with 10 ml. of water followed by successive 25 ml. portions of water. The number of 25 ml. portions necessary to remove all of the cadmium from the resin was used as an indication for the formation of anionic complexes. The results are shown in Table 1.

Table 1

Expt. No.	Resin was Saturated by:	Conc. of 10 ml. of Cd solution influent	No. of Portions
1.	3M $NaClO_4$	0.01M $Cd(ClO_4)2$	1
2.	2M Na_2SO_4	0.01M $CdSO_4$	1
3.	2M Na_2SO_4	0.01M $CdSO_4$ and 0.5M Na_2SO_4	1
4.	3M NaCl	0.01M $CdCl_2$	6
5.	3M NaCl	0.01M $CdCl_2$ and 0.5M NaCl	8
6.	3M NaI(?)	0.01M CdI_2	-

In experiment six of this series, the cadmium could not be removed at all. It was also shown that cadmium is entirely removed from a solution of cadmium iodide when it is shaken with the resin. Since these data indicate that cadmium sulfate forms an anionic complex to no greater extent than cadmium perchlorate, it seems likely that previous indications for the formation of such a species were erroneous.

Similar experiments were carried out with copper perchlorate, sulfate, chloride, and acetate, with the exception that the washing was done with successive 10 ml. portions of water. The results are given in Table 2.

Table 2

Expt. No.	Resin was Saturated by:	Conc. of 10 ml. of Cu solution influent	% Cu in successive 10 ml. portions of effluent						
			1	2	3	4	5	6	7
1.	$5\underline{M}$ $NaClO_4$	$0.01\underline{M}$ $Cu(ClO_4)_2$	5	75	20				
2.	$0.7\underline{M}$ Na_2SO_4	$0.01\underline{M}$ $CuSO_4$	15	60	25	1			
3.	$0.7\underline{M}$ Na_2SO_4	$0.01\underline{M}$ $CuSO_4$ and $0.5\underline{M}$ Na_2SO_4	35	40	20	3	0.3		
4.	$5\underline{M}$ NaCl	$0.01\underline{M}$ $CuCl_2$	10	80	10				
5.	$5\underline{M}$ NaCl	$0.01\underline{M}$ $CuCl_2$ and $0.5\underline{M}$ NaCl	15	60	25	1			
6.	$3\underline{M}$ NaAc	$0.01\underline{M}$ $CuAc_2$	5	65	25	5	1	0.1	
7.	$3\underline{M}$ NaAc	$0.01\underline{M}$ $CuAc_2$ and $0.5\underline{M}$ NaAc	0	55	30	10	3	1	0.3

For the influent in experiments 2, 3, 6, 7, Fronaeus (2) has calculated that the per cent of copper in an anionic complex is 0.1%, 80%, 0.5%, 50% respectively. Similarly for the influent in experiment 5, Bjerrum (1) has calculated that 0.02% of the copper is present as an anion. Apparently there is little formation of an anionic complex of copper sulfate, at least not as much as Fronaeus had previously assumed.

Salmon (5) used ion exchange methods to study the complexes which are formed between ferric ion and orthophosphate. Since both cationic and anionic complexes have been reported in the literature, both types of exchangers were tried. However, Permutit Zeo-Karb 225, the cation exchanger, removed nearly all of the iron from solution, but no phosphate. Either no cationic species were present, or if they were present, they were very unstable. In further preliminary studies, unsaturated solutions of iron in phosphoric acid were put through columns with the Zeo-Karb and then through the chloride form of the IRA 400. The process was then reversed. Results are summarized in Table 3. These data seem to indicate an easily displaced equilibrium between ferric ion or a cationic complex and an anionic complex.

Table 3

SOLUTION			COLUMNS		% Fe in		
$\underline{M}P_2O_5$	$\underline{M}Fe_2O_3$	Ml. Used	1st	2nd	Z.K.	IRA	Effluent
0.16	0.001	25.00	ZKH	---	100	---	---
0.16	0.001	50.00	ZKH	---	97	---	---
1.13	0.066	5.85	ZKH	ZKH	100	---	---
0.7	0.015	10.20	ZKH	IRACl	98	2	nil
1.8	0.067	5.10	ZKH	IRACl	96.5	3.5	nil
1.5	0.046	5.00	IRACl	ZKH	82	18	nil
1.13	0.066	5.01	IRACl	ZKH	79.6	18.4	2
1.8	0.067	5.00	IRACl	ZKH	82	17	1
1.13	0.066	6.00	$IRAPO_4$	ZKH	30	70	---
1.13	0.066	6.65	$IRAPO_4$	$IRAPO_4$	---	99	1
1.13	0.066	55.00	$IRAPO_4$	$IRAPO_4$	---	100	---

Further anion exchange was carried out with the phosphate form of IRA 400 which was left in contact with saturated ferric phosphate for 1-8 weeks. After filtering, the resin was washed in a column with water and then eluted with 2N HCl. The eluate was analyzed for iron and phosphate. Table 4 shows the results.

Table 4

SOLUTION				ADSORBED ON RESIN		
%P_2O_5	%Fe_2O_3	$\frac{P_2O_5}{Fe_2O_3}$	Ml. Used	mg. P_2O_5	mg. Fe_2O_3	$\frac{P_2O_5}{Fe_2O_3}$
31.3	4.77	7.37	6.00	548	181	3.4
29.1	4.95	6.60	7.25	708	238	3.4
26.6	5.31	5.65	6.70	645	260	2.8
18.0	2.25	9.01	6.00	563	179	3.5
9.08	0.59	17.3	6.01	575	143	4.5
6.07	0.11	60.5	6.00	598	76	8.8

The minimum value approached by the P_2O_5/Fe_2O_3 ratio at approximately 25% P_2O_5 was interpreted as an indication that the anionic complex under these conditions contains three phosphate groups for each iron atom. The increase beyond 25% P_2O_5 may be due to one of two things, viz., the increase in concentration of H_3PO_4 results in increasing competition of the phosphate for the resin or complexes with increasing numbers of phosphate groups may be formed.

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THE NATURE OF THE FRIEDEL-CRAFTS COMPLEX

Clayton T. Elston March 17, 1953

Since the original publications of Friedel and Crafts (1) the literature dealing with the reaction has grown to quite extensive proportions and has been the subject of numerous reviews (2). Early investigators assumed that the reaction involved an intermediate organo-aluminum compound, followed by coupling of this material with the alkyl halide. This and related theories were later shown to be untenable. Further studies also revealed that many other compounds are capable of catalyzing the reaction between alkyl halides and aromatic compounds. Examples are: $FeCl_3$, $SnCl_4$, $TiCl_4$, $BiCl_3$, $ZnCl_2$, BF_3, and H_2SO_4. In general, any compound which has strong acid character (Lewis Definition) exhibits catalytic activity. In an attempt to explain this activity the binary systems aluminum halide-alkyl halide and aluminum halide-aromatic hydrocarbon and the ternary system aluminum halide-alkyl halide-aromatic hydrocarbon, will be discussed.

Carefully purified ethyl bromide is practically nonconducting ($k = 3 \times 10^{-9}$ mhos). On the addition of $AlBr_3$ the conductivity increases with increasing concentration to about $k = 1.21 \times 10^{-4}$ mhos for a 20% solution of $AlBr_3$. Plotinkoff (3) was the first to study the electrolysis of solutions of $AlBr_3$ in ethyl bromide. Using aluminum electodes he found that metallic aluminum deposited on the cathode. Similar results were obtained by other investigators. Wertyporoch (5) studied the same system using platinum electrodes but his results were inconclusive. He found that the aluminum concentrations in the neighborhood of the cathode and anode were almost equal. He also reported that a noticeable separation of aluminum occurred at the anode. A recent study on this system has given somewhat different results (6). It was found that the principal electrode reactions are the deposition of metallic aluminu at the cathode and liberation of bromine at the anode. The aluminum concentration in the anode compartment remains almost constant; a reduction in the aluminum concentration occurs in the cathode compartment. On the basis of these data it would appear that the aluminum is present in solution in both the anionic and cationic form. The simplest explanation would involve equilibria such as the following.

$$AlBr_3 \rightleftharpoons [AlBr_2]^+ + Br^-$$

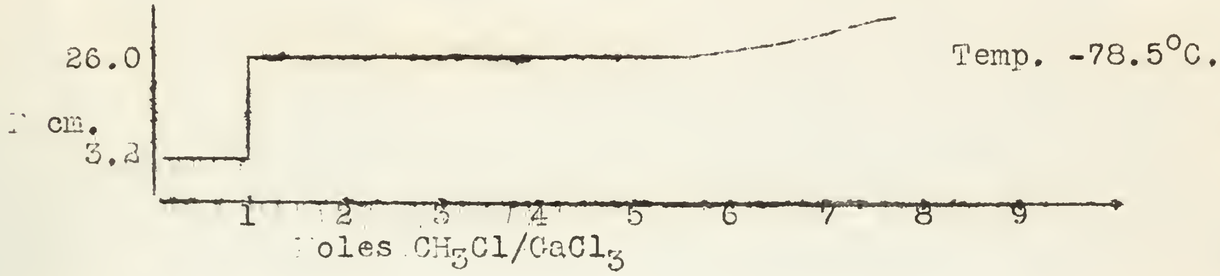
$$2AlBr_3 \rightleftharpoons [AlBr_2]^+ + [AlBr_4]^-$$

$$R\text{-}Br + AlBr_3 \rightleftharpoons R\,Br \cdot AlBr_3 \rightleftharpoons R^+ \quad [AlBr_4]^-$$

Vapor pressure studies on the system metal halide-alkyl halide have given evidence for complex formation of the type.

$$CH_3Cl + GaCl_3 \rightleftharpoons CH_3ClGaCl_3$$

Brown (7) reports the following vapor pressure-composition diagram for the system $GaCl_3$-CH_3Cl. Van Dyke (6) obtained no evidence for such complex formation with the system $AlBr_3$-C_2H_5Br but his results are inconclusive.



Positive evidence for the equilibrium, $R_3CCl + AlCl_3$ $R_3CCl \cdot AlCl_3$ is furnished by the rapid racemization of optically active alkyl halides in the presence of $AlCl_3$. Similarly when $AlCl_3$ containing labelled chlorine was used as a catalyst for the reaction of benzene with t-butyl chloride it was found that complete interchange of chlorine atoms had occurred (8).

Although several workers (6)(9) have reported the formation of complexes between aluminum halides and aromatic hydrocarbons the existence of stable complexes is still questionable. Such complexes, if formed, would appear to involve only weak attractive forces. Their role in the Friedel-Crafts reaction is uncertain but is probably a very minor one.

Benzene has a very small specific conductance ($k = 1 \times 10^{-13}$ mhos at 25°C.) and upon addition of aluminum halide there is no noticeable increase in conductivity. However, addition of alkyl halide or halogen acid to such a solution produces a very marked change (10). The solution becomes colored and as the concentration of the alkyl halide (or halogen acid) is increased a second liquid phase separates. The lower phase is highly colored and strongly conducting ($k = 1 \times 10^{-2}$ mhos) while the upper phase is only slightly colored and weakly conducting ($k = 1.9 \times 10^{-5}$ mhos). The reactions involved were found to be reversible since removal of the halogen acid yielded a homogeneous system which could be further separated into pure aluminum halide and hydrocarbon.

In studying the system aluminum chloride-toluene-hydrochloric acid, Brown (11), found that $AlCl_3$ dissolves in toluene in the presence of HCl to give a brilliant green solution. Relating solubility of $AlCl_3$ to the pressure of HCl above the solution at -80°C. they found that as a limiting case approximately one mole of HCl is taken up for each mole of $AlCl_3$ which goes into solution. At -45°C. one mole of HCl is taken up for every two moles of $AlCl_3$. They suggest that the Friedel-Crafts complexes are organic salts of the hypothetical acids $HAlCl_4$ and HAl_2Cl_7. The high solubility of $AlCl_3$ in such complexes would tend to indicate that complexes of

$$Ar + HCl + AlCl_3 \rightleftarrows ArH^+ AlCl_4^-$$

a higher order are also possible. The general formula would be $ArH^+ [Al_nX_{3n+1}]^-$. It should be noted that results of various workers (7)(8) have shown that there is no evidence for an acid of the type $HAlCl_4$ or $HAlBr_4$. Studies of the system AlX_3-HX over a wide range of temperatures (-120° to 300°C.) revealed that the pressure of HX is not affected by the presence of AlX_3. It would thus be extremely improbable if a detectable concentration of the free acid could exist under the conditions of the Friedel-Crafts reaction. The exchange between labelled $AlCl_3$ and HCl at low temperatures offers a means of estimating the equilibrium concentration of $HAlCl_4$ and such an investigation is now being conducted by Professor Benson

$$AlCl_3^* + HCl \rightleftharpoons AlCl_3 + HCl^*$$

at the University of Southern California.

The electrolysis of the ternary complex aluminum bromide-ethyl bromide-benzene using an aluminum anode has been shown to be an efficient method for aluminum plating (12). The overall electrode reaction is the solution of aluminum at the anode and the deposition of aluminum at the cathode. It seems reasonable to assume that $AlBr_3$ could behave as a 1:3 electrolyte when dissolved in the highly polar complex phase. Wertyporoch (5) studied electrical transference in the system aluminum bromide-ethyl bromide-hexaethylbenzene and found that aluminum concentrates in the anode compartment, while bromine and hexaethylbenzene concentrate in the cathode compartment. Such data substantiate the formulas proposed by Brown.

Brown (11) assumes that the formation of the ternary complex is involved in the rate-controlling step of the Friedel-Crafts reaction. The highly polar complex phase, which is capable of dissolving an excess of any of its three components would presumably furnish an excellent medium for the ionic reactions involved.

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ACID-BASE BEHAVIOR IN INERT SOLVENTS

March 24, 1953 Daryle H. Busch

Introduction. At the turn of the century, the ionization theory of acids and bases was commonly believed to apply to all solvent systems. Substances such as hydrogen chloride were not considered to be acids in solvents which produced no ions. In 1902, Kahlenberg (31) reported several ionic type reactions in benzene. Shortly thereafter, Vorlander (45) carried out the titration of aniline with hydrogen chloride in benzene using methyl yellow as an indicator. These and similar developments led a number of investigators to suspect that ionization is not a necessary condition for acid character.

Methods Employed in the Study of Acids and Bases in Aprotic Media.

Hantzsch was of the opinion that a more broadly valid criterion for acid strength than "hydrogen ion concentration" could be found in the relative tendencies of acids to form salts with indicator bases. A technique was developed for describing the relative strengths of acids in terms of the stabilities of such salts. (21)(22)(29) Hantzsch and his co-workers also measured the catalytic effects of different acids on the rate of inversion of succrose and the rate of decomposition of diazoacetic ester and related these rates to the intrinsic strengths of the acids. (21)(22)(26) They found that the acids were commonly stronger in this respect in inert solvents such as benzene and chloroform than in basic media like water.

The investigations carried out by LaMer and Downes (36)(37)(38) are especially significant in demonstrating the use of indicator methods in determining the relative strengths of acids and bases in aprotic media. In the ideal case, HA is considered to react with a base B to produce a much weaker acid HB in the presence of an indicator I. The indicator is partially converted to its acid form HI. From a consideration of the acidity constants for the acids HA, HB, and HI the following expression is derived:

$$\log [A]/[HA] = \log [I]/[HI] - pK_{HA} + pK_{HI}$$

A plot of log [A]/[HA] against log [I]/[HI] then gives a family of parallel straight lines with unit slopes whose intercepts on the log [I]/[HI] axis give a measure of the strengths of the acids as compared to the indicator HI.

An extensive investigation of the reaction of various organic bases with indicator acids in inert media has been undertaken by Davis and her associates. The technique employed is best characterized as a spectro-photometric titration of an indicator acid with a basic material. The relative strengths of a series of bases have been determined and association constants corresponding to the reaction shown below were measured.

$$B + HA \rightleftharpoons BH^{+}\ldots A^{-}$$

Two indicators were synthesized during the early phases of these studies (9); bromphthalein magenta E (tetrabromophenolphthalein

ethyl ester) and bromphthalein magenta B (tetrabromophenolpthalein n-butyl ester). These indicators are more soluble in aprotic media and often give simpler color changes (10) than the more familiar indicators.

A parameter representing the true strengths of bases in combination with a standard indicator acid is found in the association constant, K_a, for the reaction mentioned above.

$$K_a = \frac{[BHA]}{[B][HA]}$$

From this expression the equation below is obtained.

$$\log [BHA]/[HA] - \log [B] = \log K_a$$

The association constant may be evaluated by plotting log [BHA]/[HA] against - log [B]. In order for K_a to be valid, the plot should be a straight line with a negative slope equal to unity. The validity of the results may be judged from Table 1 below. (9)

Table 1

Organic Base	Log K_a	K_a	Slope of Curve
di-n-butylamine	4.19	1.5×10^4	-1.17
triethylamine	4.36	2.3×10^4	-1.03
piperidine	5.08	1.2×10^5	-1.08
diphenylguanidine	5.35	2.2×10^5	-1.03
ditolylguanidine	5.80	6.3×10^5	-1.23

Another type of information which has been obtained by Davis et al stems from the nature of the color changes which the indicator undergoes upon addition of a base. These color changes provide some insight into the nature of the chemical reactions which are taking place. All of the changes observed may be explained on the basis of three assumptions:
1. The yellow color of solutions of bromphthalein magents (BPM) in aprotic media is characteristic of the neutral, unsolvated, and non-ionized acid form of the indicator. 2. The blue color of solutions of tetraalkylammonium salts of BPM in aprotic solvents is characteristic of the BPM anion when it is associated with the positive constituent of the salt only through coulombic attraction. 3. The magenta color of solutions of BPM containing an excess of a tertiary amine is characteristic of a highly polar addition compound formed by incomplete removal of the proton from the indicator anion (a hydrogen bridge exists between the amine and the anion).

The shift in color from that represented by the primary addition compound formed by a primary, secondary, or tertiary amine with the acid indicator to the color characteristic of the coulombically bonded tetraalkylammonium salt in basic solvents or upon the addition of a small amount of a basic solvent to a solution in an inert medium may be explained similarly with the generalized mechanism.

$$B + HA \rightleftharpoons BH^{+}\ldots A^{-} \quad + \quad B' \rightleftharpoons (BH^{+}\ldots B')\,A^{-}$$

It also follows that the stability of the color characteristic of the primary reaction, when an indicator acid is dissolved in a basic solvent of very large steric requirements, stems from the reaction of one molecule of base to form a highly polar addition compound whose hydrogen bridge is so shielded by the large solvent molecule that the secondary reaction, breaking of the hydrogen bond between the anion of the acid and the cation by the action of the second solvent molecule, cannot be accomplished. This sort of phenomenon finds support in the studies of Brown and his co-workers who showed that when the steric requirements of an acid and base pair are too large no reaction can occur. (9)(18)

Theoretical Significance of Studies in Aprotic Solvents. Although it is probable that no solvent of practical value is completely devoid of acidic or basic character, solvents such as hydrocarbons halogenated and partially halogenated hydrocarbons may be considered to have neither acidic nor basic properties since their relative tendencies to behave either as acids or as bases are much smaller than is the case with the substances which are under study.

The factor which would be most significant in its effect on the measurable properties of acids and bases and their salts in aprotic media is the dielectric constant of the solvent. The effect of dielectric constant on the behavior of acids and bases and their salts has been studied by Bronsted, (7) by Hammett, (20) and by Kraus and Fuoss. (32) Kraus (34) reported that the properties of an acid in an inert solvent are largely dependent on the quantum forces between the proton and the anion. The role played by the dielectric properties of the solvent was found to be relatively slight. Other investigators (1)(2)(16) report that a solvent of higher dielectric constant than is known would be required to dissociate an acid without the formation of a new chemical bond. Kraus (34) and Hammett (20) have shown that the degree of dissociation of a salt depends on the dielectric constant of the medium. In benzene, ion pairs would be expected to form. (4)(33) The interionic attraction theory relates the dielectric constant of the medium to activity coefficients. (3)

The Mechanism of Acid-Base Reactions. Bronsted (7) envisions the combination of two hypothetical half reactions to produce neutralization. No mechanism for the exchange of the proton is offered.

The Lewis theory arrives at the same final result by presuming that the reaction involves contact of the Base A with the acid HB. The intermediate compound is supposed to have only a transient existence since it is considered unrealistic to suppose that a proton can share two pairs of electrons simultaneously. (39)

Demonstration of the formation of the hydrogen-bonded addition compound as the first product of the reaction of a hydrogen acid with an amine provides a link between the Lewis and Bronsted theories In fact, this scheme presents a unique case of neutralization in the Lewis concept only because of the high polarity of the compound formed. The evidence cited in support of the existence of this addition

compound is:(13) (a) Ionization is unimportant in the reaction; (b) It is possible to calculate an equilibrium constant for the reaction assumed; (c) Spectrophotometric evidence makes it possible to identify the species with the conditions under which it exists; (d) The "salts" formed in these reactions have dipoles quite similar to those found for the more obvious products of Lewis acid-base reactions.

The two-stage mechanism proposed by Davis and co-workers is represented by the scheme below.(13)

$$R_3N + \underset{\text{yellow}}{HI} \rightleftharpoons \underset{\text{magenta}}{R_3NH^+ \ldots I^-}$$

$$\underset{\text{magenta}}{R_3NH^+ \ldots I^-} + R_3N \rightleftharpoons \underset{\text{blue}}{(R_3NH^+ \ldots NR_3)I^-}$$

The first equation represents the formation of a hydrogen bond. The second equation represents rupture of the old hydrogen bond, which joined equal and opposite charges, and the formation of a new hydrogen bond with the incidental effect that ion pairs are produced.

From less thorough investigations, the effect of acid molecules on the process of neutralization may be inferred. Maryott (40) observed that an excess of acid increases the conductance of solutions of salts of carboxylic acids and sulfonic acids in inert media. The effect is too sensitive to be attributed to the change in dielectric constant of the solution accompanying salt formation. Since cryoscopic data(42) obtained for a related system indicates complex formation between carboxylic acids and their salts in inert solvents, it was proposed that the anion, $RCOO^-$, of the salt forms a dimer with a molecule of acid. The species formed would be somewhat analogous to the ordinary dimeric structure of the free acid in an inert solvent.

Inasmuch as no solvent has been found which possesses acidic but not basic properties and since autoprotolysis of such strong acid solvents as sulfuric acid and hydrofluoric acid has been demonstrated (3) the scheme appears to be quite reasonable. This leads to the conclusion that the dissolution of a base in an acidic solvent follows a two step equilibrium.

The Relative Strengths of Acids and Bases. The recognition that water and other basic solvents exert a leveling effect(18)(25) on the strengths of acids in solution has been instrumental in causing various investigators to study acid strengths in aprotic solvents The leveling effect may be demonstrated by the addition of water to solutions of various acids (29) in aprotic media. Such an experiment would reveal that the relative acidities of the weaker acids are increased while those of the stronger acids are decreased. In gener the restriction posed by the leveling effect is that no acid may exist in a basic solvent whose proton donating tendency exceeds that of the onium ion of the solvent. It is obvious in view of this limitation that the strengths of the stronger acids must be measured in solvents of very slight basic character.

The most common method of measurement of the strengths of acids in aqueous solutions is by determining the electromotive force with an electrode reversible to hydrogen. The electrode potential as a criterion for acidity is independent of the interpretation given to it by the Bronsted theory. It is the activity of hydrogen which is measured in this manner, and this activity is not necessarily parallel with the concentration of hydrogen or hydronium ions. It is, to the contrary, a measure of the reversible work required to transfer a proton from one given base to another. In the ideal case, (5)(20)(38) the hydrogen electrode potential would provide the means for extending the precise measurement of acid and base strengths to all solvents. This is not feasible at the present because of such complicating factors as liquid junction potentials (22)(23) and individual ion activities.(24)

In attempting to measure the relative strengths of acids in aprotic media, methods based on colorimetric or spectrophotometric techniques have proven most fruitful.(6)(17)(21)(28)(38) The formulation most often used is essentially that given by LaMer and Downes; this analysis follows the Bronsted theory. Table 2 lists series of acids in the order of their decreasing strengths as observed by several investigators. The values of pK are given for two of the series. These parameters differ in their numerical values primarily because different arbitrary standards were chosen by the respective investigators. The general trends are the same.

LaMer and Downes(37)(38) have demonstrated an ingenious technique for setting up a series of relative acid strengths based on indicator studies in inert solvents. This method also involves the Bronsted scheme for the acid-base reaction. These investigators found that their indicator method was limited, for any given indicator, to those acids whose pK values differed by plus or minus one unit, or less, from the pK value of the indicator. They then pointed out that, if the relative acidities of two indicator systems could be established, the acid systems studied with these two indicators could then be compared. For example, dichloroacetic acid is weaker than dimethyl yellow but stronger than bromphenol blue. The experimental curves for these two indicators can then be displaced along the log [I]/[HI] axis of a graph of log [A]/[HA] against log [I]/[HI] until they become continuous. By a stepwise correlation of indicators in this manner it is possible to establish a complete numerical scale for all the acids.

A number of investigators (4)(14)(15)(27)(28)(30)(35) have concluded that the primary reaction which takes place between a base and a proton acid culminates in the formation of a highly polar addition compound. The extent to which this reaction proceeds may be measured and an equilibrium constant may be calculated. Table 3 lists the systems which have been studied and gives the association constants for this primary reaction.

Table 2

Relative Acid Strengths

Investigator	Bronsted(6)	Hall(19)	Hantzsch(21)(22)	Hantzsch(2
Method	Indicator	pKd	Indicator	Inversion of Sugar
Solvent	Benzene	Water	Chloroform	Water
	hydrochloric	-7.4	perchloric	hydroiodic
	methyl red	4.9	sulfonic acids	perchloric
	dimethyl yellow (ion)	3.5	hydrobromic	hydrobromic
	trichloroacetic	0.7	hydrochloric	benzenesulfonic
	dichloroacetic	1.3	nitric	hydrochlori
	picric	0.3	trichloroacetic	nitric
	o-nitrobenzoic	2.3	tribromoacetic	trichloroacetic
	chloroacetic	2.9	maleic	sulfuric
	salicylic	3.0	malonic	chloroaceti
	bromphenol blue	4.1	chloroacetic	formic
	b-dinitrophenol	3.7	a-bromopropionic	acetic
	o-chlorobenzoic	2.9	bromoacetic	
	neutral red (ion)	6.9	formic	
	m-chlorobenzoic	3.8	b-iodopropionic	
	bromcresol green	4.7	acetic	
	benzylammonium ion	9.4		
	formic	3.7		
	phenylacetic	4.3		
	benzoic	4.2		
	acetic	4.7		
	isoamylammonium ion	10.6		
	bromcresol purple	6.3		
	piperidinium ion	11.1		
	bromthymol blue	7.0		

Investigator	LaMer and Downes(38)		Griffiths(17)	
Method	Indicator		Indicator	
Solvent	Benzene		Chlorobenzene	
	Acid	pK	Acid	pK
	methyl red	0.55	bromphenol blue	3.46
	trichloroacetic	0.55	trichloroacetic	3.37
	propyl red	0.7	dichloroacetic	2.52
	dimethyl yellow	0.8	chloroacetic	0.77
	dichloroacetic	1.7	salicylic	0.74
	salicylic	2.6	dinitrophenol	0.00
	chloroacetic	2.8	benzoic	-0.58
	bromphenol blue	3.2	acetic	-1.00
	bromcresol green	3.4	propionic	-1.08
	formic	3.7		
	benzoic	4.5		
	neutral red	4.6		
	acetic	5.2		
	diethylammonium ion	5.5		

Table 3

Association Constants, K_a, and Dissociation Constants, K_d, for Primary Acid-Base Reactions in Inert Solvents.

ase	Acid	Solvent	K_a	K_d
ribenzylamine(11)	trinitro-m-cresol	benzene	450	--
riphenylguanidine (13)	bromphthalein magenta E	benzene	525	--
ribenzylamine(11)	picric acid	benzene	1,600	--
i-n-butylamine(9)	bromphthalein magenta E	benzene	15,500	--
riethylamine(9)	bromphthalein magenta E	benzene	23,000	--
riethylamine(9)	bromphthalein magenta B	benzene	23,000	--
iperidine(9)	bromphthalein magenta E	benzene	120,000	--
iphenylguanidine(13)	bromphthalein magenta E	benzene	220,000	--
iphenylguanidine(9)	bromphthalein magenta B	benzene	220,000	--
i-o-tolylguanidine(9)	bromphthalein magenta E	benzene	860,000	--
i-o-tolylguanidine(9)	bromphthalein magenta B	benzene	860,000	--
,N-dimethylaniline(12)	hydrogen chloride	$CHCl_3$	67,000,000	--
niline(35)	picric acid	$C_6H_5NO_2$	125	2x10^{-5}
imethylaniline(35)	picric acid	$C_6H_5NO_2$	4,000	4.1x10^{-}
yridine(35)	picric acid	$C_6H_5NO_2$	61,300	5.54x10
rimethylamine(41)	sulfur dioxide	benzene or $CHCl_3$	525	--

Equilibrium Constants, K_2, for the Secondary Reaction of Acids and Bases

ase	Acid	Solvent	K_2
iphenylguanidine(14)	bromphthalein magenta	benzene	13.5
riphenylguanidine(14)	bromphthalein magenta	benzene	22.5

A second measurable equilibrium has been demonstrated by Davis and Hetzer.(13)(14) This equilibrium measures the extent to which the addition compound $BH^+...A^-$ is solvated and dissociated into ion pairs by one mole of base B', which may be the same as or different from the base B. The values of the equilibrium constants reported for the two secondary reactions studied by Davis and Hetzer are listed in Table 3.

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METAL-DIAMINE CHELATE COMPOUNDS CONTAINING HIGHER-MEMBERED RINGS

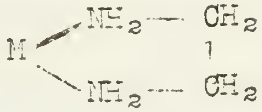
William E. Cooley March 31, 1953

I. Introduction

It is well known that nitrogen atoms in amines readily act as electron pair donors in coordinating with certain metal ions. Many stable complex compounds contain coordinated ammonia or amine molecules. Even greater stability results from coordination of ethylenediamine or its homologs, since formation of a chelate ring takes place. Chelate rings having five or six members appear to be much more stable than larger rings, with respect to their resistance to hydrolysis in water solution and decomposition by heat.

II. Five-membered Rings

Ethylenediamine (en) and substituted ethylenediamines form five-membered chelate rings with metal ions.



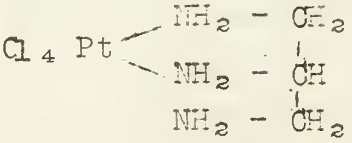
M= Co, Cr, Pt, Ni, Cu, Fe, etc.

Substituted groups on the carbon atoms of ethylenediamine usually have little effect on the color, stability, or method of preparation of these complexes. Solubility in water is sometimes increased by the addition of such groups; the propylenediamine (pn) and 2, 3-butylenediamine (bn) complexes of cobalt are more soluble than their ethylenediamine homologs. (1) Cyclopentanediamine (1), cyclohexanediamine (5), iso-butylenediamine (ibn) (9), and meso-stilbenediamine (1) have also been used as chelating ligands.

III. Six-membered Rings

Increasing to three the number of carbon atoms between the amine groups lowers the stability of diamine chelates. Pfeiffer and Haimann (10) were unable to prepare chromium complexes with trimethylenediamine (tn) by the same reaction which they found to give good yields of ethylenediamine and propylenediamine chelates. Bailar, Rollinson, and Work (1, 15) likewise found that anhydrous ethylenediamine and anhydrous chromium (III) sulfate react to form $[Cr\ en_3]_2(SO_4)_3$, but that anhydrous trimethylenediamine does not undergo a parallel reaction.

Mann and Pope (7) resolved into its optical antipodes the chelate compound $[Cl_4\ Pt\ NH_2\ CH_2\ CH\ (NH_2)\ CH_2\ NH_2]$. Resolution of this compound is possible only if it has a 5-ring structure.



Coordination in the 1 and 3 positions would yield a symmetrical 6-ring.

It is possible, however, to produce six-membered chelate rings. Tschugaeff (17) reported that addition of trimethylenediamine to nickel disuccinimide 8-hydrate resulted in the formation of a violet, water-soluble complex compound, $[Nitn_3]$ (succinimide)$_2$ · $2H_2O$. Also prepared by Tschugaeff (19) were the blue-violet crystalline compound $[Ni\ tn_2]SO_4$ and the unstable red-violet $[Nitn_3]SO_4$. The chloroplatinite salt of $[Nitn_3]^{++}$ is more stable and may be formed from nickel (II) chloride in water solution, trimethylenediamine, and potassium chloroplatinite.

Werner(21) prepared bis-trimethylenediamine complexes of cobalt (III) by the same methods used for bis-ethylenediamine complexes.

Tschugaeff(19) and Drew and Tress(4) found that addition of trimethylenediamine to a water solution of potassium chloroplatinite at room temperature produces yellow $[Pttn\ Cl_2]$. At higher temperatures $[Pttn_2][Pt\ Cl_4]$ is formed.

Breuil(2) added trimethylenediamine to ferrous chloride, ferrous bromide, and ferrous iodide in anhydrous methyl alcohol. With the work carried out in a hydrogen atmosphere, the corresponding tris-diamine complexes, $[Fetn_3]X_2$, were formed. These compounds decompose in air.

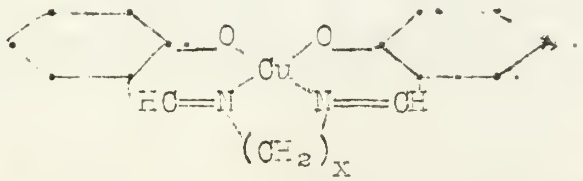
Bailar and Work(1) have prepared trimethylenediamine complexes of cobalt, noting that $[Cotn_3]^{+++}$ may be prepared only in the presence of a catalyst, such as activated charcoal. Otherwise carbon dioxide from the air forms carbonate ions, which coordinate more readily than the diamine, yielding $[Cotn_2\ CO_3]^+$.

Chelates containing six-membered rings have also been prepared with 2, 2-dimethyltrimethylenediamine(1), 1-methyltrimethylenediamine (6), and 2, 4-diaminopentane.(3,19)

IV. Rings of More Than Six Members.

Tschugaeff (17,18), Werner(21), Drew and Tress(4) and Pfeiffer and Haimann(10) attempted to form chelates containing tetramethylenediamine and pentamethylenediamine. Their efforts resulted in the formation of insoluble residues, products without fixed compositions, or metal hydroxides. In some instances no reactions at all took place. Pfeiffer and Lübbe(12) also were unable to form chelates of seven and eight-membered rings. These investigators studied decamethylenediamine and octadecamethylenediamine as well, but no chelates were obtained. McReynolds(8) found that coordination takes place between decamethylenediamine and cupric ions, but there is no indication of the presence of chelates.

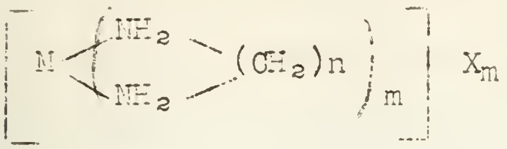
Pfeiffer(11) succeeded in forming such complexes as



x=4, 5, 10

in which a large ring is stabilized by the presence of two six-membered rings.

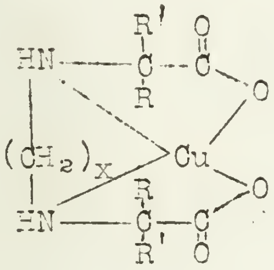
Pfeiffer, Schmitz, and Böhm(14) have recently reported success in stabilizing diamine chelate rings of more than six members. Using alcohol and ether solutions as reaction media, these workers have isolated crystalline compounds whose composotions correspond to


$\left[M\left(NH_2(CH_2)_nNH_2\right)_m\right]X_m$

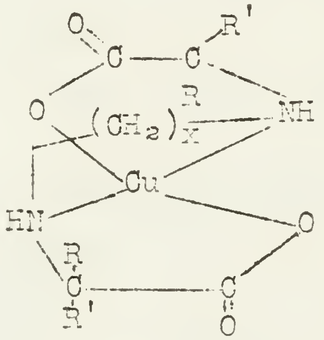
$M = Cu^{++}, Ni^{++}, Zn^{++}, Hg^{++}, Cd^{++}$ (m=2) and Ag^{+} (m=1).
n = 4, 5, 6.
x = ClO_4^-, β-$OSO_2C_{10}H_7^-$, NO_3^-

The mercury and silver compounds are usually colorless and in some cases may be recrystallized from hot water. The copper and nickel compounds are blue and blue-violet; in general they decompose rapidly in water. The authors state that these compounds form upon merely mixing the metal salts and diamines in alcohol or ether, then evaporating the solvent. The absence of water molecules appears to lessen competition with the amine groups for coordination positions.

The work of Schlesinger(16) suggests another possible structure for the compounds prepared by Pfeiffer and his associates. Schlesinger found that the inner complexes of copper with *bis*-imino acids, $[Cu(CH_2)_x-(NHCRR'COO)_2]$, have the blue color, general solubility in water, and characteristic conductivity of copper-amino acid complexes if x is 2 or 3. If x is 10, the *bis*-imino acid complexes are violet and only slightly soluble. For intermediate values of x, both forms appear. Schlesinger assumed that *cis*-*trans* isomerism is present, with the longer molecular chains spanning the *trans* positions and the shorter chains being confined to the *cis* positions, as in the amino acid complexes.



cis Form



trans Form

V. Diamines as Metal Deactivators

Small amounts of metals, especially copper, have been found to be powerful catalysts for autoxidation of petroleum products and many other organic compounds. Complexing agents function as metal deactivators, reducing the catalytic effect by forming stable complexes with the metals present. In the case of diamines, deactivation ability falls off rapidly as the number of carbon atoms separating the amine groups increases beyond three. This tendency reflects the greater stability of five- and six-membered chelate rings.(20)

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Cyclopentadienyl Complexes

Victor D. Aftandilian

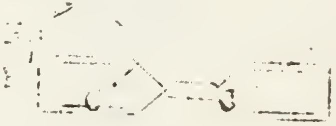
April 7, 1953

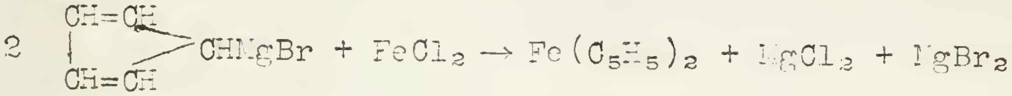
Gringnard reagents have been shown (1) to form hydrocarbons by the coupling reaction:

$$2RMgX + MX_2 \rightarrow R\text{-}R + 2MgX_2 + M$$

Brown and Lichtenwalter (2) obtained an almost quantitative yield of biphenyl from phenylmagnesium bromide and ferric chloride. Ferric chloride is initially reduced to ferrous chloride by the Grignard reagent, which in turn reacts with the excess of the reagent to form biphenyl. Several mechanisms have been proposed for this reaction, the most feasible one being that offered by Krizewski and Turner(10). They postulated that probably unstable organometallic intermediate compounds are formed, which decompose giving hydrocarbons and the free metal as shown below:

$$2RMgX + MX_2 \rightarrow R\text{-}M\text{-}R + 2MgX_2$$
$$R\text{-}M\text{-}R \rightarrow R\text{-}R + M$$

As a possible route to fulvalene () synthesis, Keally and Pauson (9) applied this reaction to cyclopentadienylmagnesium bromide, but instead obtained bis-cyclopentadienyliron(II).



$$2\ \begin{array}{l}CH{=}CH\\ |\\ CH{=}CH\end{array}\!\!>CHMgBr + FeCl_2 \rightarrow Fe(C_5H_5)_2 + MgCl_2 + MgBr_2$$

Less than a month before this discovery was reported, Miller and co-workers (11) prepared $Fe(C_5H_5)_2$ by passing gaseous cyclopentadiene over reduced iron in nitrogen atmosphere at 300° and atmospheric pressure. The formation of bis-cyclopentadienyliron(II) proceeds only for 10-15 minutes, after which further reaction is only effected after careful oxidation and re-reduction of iron at 450° C and in an atmosphere of nitrogen containing steadily increasing proportions of oxygen, and finally air. Kaplan and co-workers (8) modified the Keally and Pauson procedure by the addition of one-third of a molar equivalent of ferric chloride to cyclopentadienylmagnesium bromide, both in tetrahydrofuran, and obtained 51% yield.

Some of the physical properties of bis-cyclopentadienyliron(II) are listed in Table I.

Table I.

Physical Properties of Bis-cyclopentadienyliron(II) or "Ferrocene" *

Formula	$Fe(Cp)_2$**		
Formula weight	186		
Melting point, °C	173-174		(9)
	172.5-173		(10)
Boiling point, °C	249		(8)
Triple point, °C	183		(8)
Vapor pressure of the solid	$\log P_{mm} = 7.615 - \frac{2470}{T}$		(8)
Vapor pressure of the liquid	$\log P_{mm} = 10.27 - \frac{3680}{T}$		(8)
Heat of sublimation of the solid	16.81	kcal/mole	(8)
Heat of vaporization of the liquid	11.3	kcal/mole	(8)
Heat of fusion	5.5	kcal/mole	(8)
Heat of formation	25.6	kcal/mole	(8)
Trouton's constant	21.2		(8)
E^o_{298} $Fe(Cp)_2 \rightleftharpoons [Fe(Cp)_2]^+ + \bar{e}$	-0.56***		(12)
(in acidic solution)	-0.59***		(16)
Bond distance, A°			
C-C	1.41		(5)
Fe-C	2.0		(5)

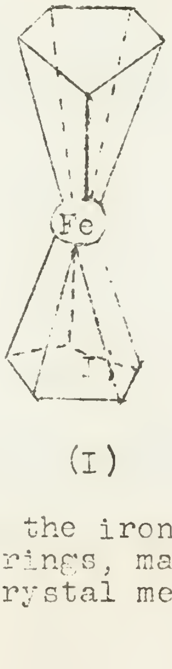
---

* Woodword and co-workers (17) proposed this name.

** The symbol Cp, representing cyclopentadienyl unit, will be used in this abstract.

*** Latimer convention.

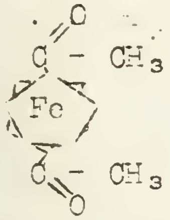
The infrared absorption spectrum of ferrocene shows a single band at 325[illegible], which indicates the presence of only one type of C-H bond in this compound. Wilkinson etal (16) proposed structure (I) for ferrocene based upon the above observation.



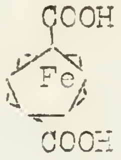
(I)

This structure, in which the iron atom is symmetrically placed between two cyclopentadienyl rings, making a "sandwich" type molecule, has been confirmed by x-ray crystal measurements. (5 and 6). In spite

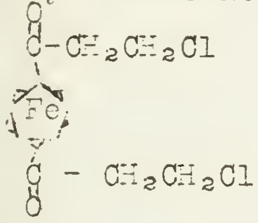
of its high degree of formal unsaturation, ferrocene does not possess properties typical of polyolefinic substances. For example, it does not react with maleic anhydride in boiling benzene; it is not hydrogenated under normal conditions over reduced platinum(II) oxide; it is resistant to the action of acidic reagents, and has high thermal stability. Woodward and co-workers(17) carried out several typical aromatic reactions with ferrocene and reported the following organic derivatives:



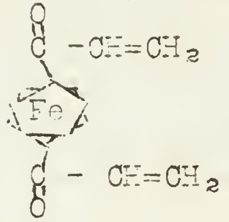
diacetylferrocene



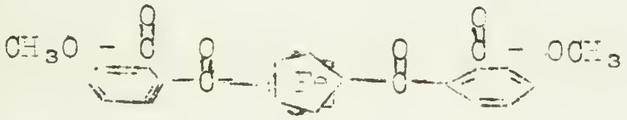
ferrocenedicarboxylic acid



bis-β-chloropropionylferrocene



bis-acryloylferrocene



dimethyl ester of bis-o-carboxybenzoylferrocene

Perhaps a more convincing proof for the aromaticity of ferrocence is the striking resemblance of the infrared absorption spectra of its derivatives to those of **benzene.**
(See Table II).

Table II Infrared Band Positions for Opposite Cases

	R=ferrocenyl	R=phenyl
	μ	μ
H-R	3.26	5.27
CH_3CO-R	5.97	5.93
$CH_3O\overset{O}{C}-R$	5.82	5.81
o-$CH_3OOC-C_6H_4-\overset{O}{C}-R$	6.02	5.97

Even greater interests are the ionization constants for the carbaxylic acids, measured in two-to-one ethanol to water solutions.

Ferrocene dicarboxylic acid	pK_1	$3.1x10^{-7}$
	pK_2	$2.7x10^{-8}$
Benzoic acid	pK_1	$2.7x10^{-7}$

Woodword etal (17) postulated that "the very small differences between the two dissociation constants of ferrocene dicarboxylic acid indicates that the carboxyl groups interact very little, and must be very far apart, while the near identity of the first constant with benzoic acid demonstrates that the ring carbon atoms of ferrocene, and thence, necessarily the central iron atom as well, are subsequently neutral." This observation is of importance with respect to the detailed electronic structure of ferrocene, since it excludes any form of hybridization which leads to charge separation within the molecule. For example, the possibility of coordination of iron with 18 electrons (five from each cyclopentadienyl unit, plus 8 from the iron) to have effective number of 36, krypton structure, as in the case of ferrocyanide, is ruled out. In addition to the objection that the aromatic properties of ferrocene make it seem most unlikely that all the electrons of the cyclopentadienyl rings can be involved in the filling of the orbitals of the metal atom, it seems that a high negative charge would also be placed on the central metal atom and this was shown not to be the case in the determination of the ionization constants of ferrocence dicarboxylic acid. At present there is not sufficient evidence to predict the actual electronic structure of ferrocene. Eiland and Pepinsky (5) are investigating the nature of the bonding and the electronic configuration of the iron atom in ferrocene by a method of three-dimensional analysis.

Ferrocene is readily oxidized to the blue $[Fe(Cp)_2]^+$ cation. Oxidation may be effected anodically, by air in presence of acids or by halogens, by ferric chloride or ceric sulfate. Especially convenient are aqueous silver sulfate or p-bezoquinone in organic solvent in the presence of acids. The ferricinium ion is reduced by stannous chloride. Ferricinium ion has been isolated in the form of crystalline salts: $[Fe(Cp)_2]GaCl_4$, $[Fe(Cp)_2]$picrate, and $[Fe(Cp)_2]ClO_4$. [illegible]

In view of the above postulations concerning ferrocene, it was to have been expected that ruthenium (II) and cobalt (III), both of which are isoelectronic with iron(II), and also other transition elements, which have available d orbitals, would form similar complexes. Table III lists the cyclopentadienyl complexes which have been reported in literature to date.

Table III
List of Cyclopentadienyl Complexes.

Complex	Special Name	References
$Fe(Cp)_2$	Ferrocene	8, 9, 11
$[Fe(Cp)_2]^+$	Ferricinium ion	16
$Ru(Cp)_2$	Ruthenocene	13
$[Ru(Cp)_2]^+$	Ruthenicinum ion	13
$[Co(Cp)_2]^+$	Cobalticinium ion	14
$Ni(Cp)_2$		15
$[Ti(Cp)_2]^{++}$		15
$[Ti(Cp)_2]^+$		15
$[Zr(Cp)_2]^{++}$		15
$[V(Cp)_2]^{++}$		15

Cyclopentadienyl complexes have opened an interesting field of study in inorganic chemistry; intensive investigations are being conducted to determine their structures, to study their properties, and to find uses for these compounds.

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Disulfur Heptoxide

April 14, 1953 A. B. Galun

M. Berthelot(1,2,3) was the first to describe a material which he called "acide persulfurique". It was obtained by passing either sulfur dioxide or sulfur trioxide mixed with oxygen through an electric discharge. The product was considered to be a compound of heptavalent sulfur. However, Mendelejeff(4) pointed out that this compound must be a peroxide. H. Giram(5) calculated the heat of formation:

$$S_2O_7 \rightarrow 2SO_3 + 1/2\ O_2 + 9.7\ \text{cal.}$$

A. Moser(6) found later (1910) that S_2O_7 could be prepared in a discharge tube even at 70°C (Berthelot claimed it decomposed at room temperature). F. Meyer et al(7) repeated Berthelot's experiments in 1922 and obtained products corresponding to the formula S_3O_{11}. They assumed the material to consist of a mixture of SO_3 and SO_4 and claimed that Berthelot's compound was of the same composition. This point of view was supported by T. Maisin(8) who obtained the same compound in 1928.

Pure SO_4 was prepared by R. Schwarz and H. Achenbach(9) in 1934; mixtures of SO_3 and SO_4 were also characterized(10). V. Wannagat and G. Mennichen(11) prepared pure S_2O_7 and have characterized it chemically. The results of their investigations are summarized in the discussion which follows.

Method of Preparation: A discharge tube was evacuated and filled up to a certain pressure with SO_2. The tube was immersed in liquid air to freeze out the SO_2, and then filled with oxygen gas. The gases were allowed to mix overnight at 20°C, and a discharge of about 1mA and 11KV was passed through the tube. A solution of $CaCl_2$ was used as "coating liquid". A solid separated as a film on the walls of the discharge tube.

Berthelot assumed that nitrogen prevents the crystallization of S_2O_7 but does not interfere with its formation. The authors repeated the experiments in presence of nitrogen and obtained a product which proved to be $(NO)_2\ S_2O_7$ (12). A. Moser(6) also carried out his experiments in presence of nitrogen.

If equal volumes of SO_2 and O_2 are employed, and S_2O_7 is formed according to the equation: $4SO_2 + 3O_2 \rightarrow 2S_2O_7$ (solid), the gas volume should decrease to 1/8 that of the original. It was found that the pressure does drop as shown in figure 1, but never to $P_o/8$.

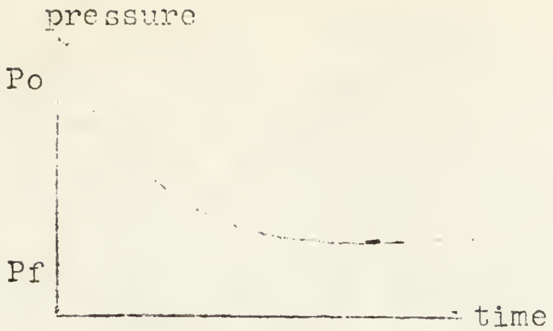


Figure 1

The residual gas was found to contain SO_3 and SO_2 but no S_2O_7. It was concluded that several equilibria established under discharge conditions: $S_2O_7 \rightleftarrows 2SO_3 + 1/2\ O_2$ and $SO_3 \rightleftarrows SO_2 + 1/2\ O_2$. This postulate was confirmed by subjecting S_2O_7 (which is quite stable up to $40^\circ C$) to a discharge in a closed system and measuring the pressure. It was found that under discharge conditions S_2O_7 always assumes the same final pressure irrespective whether the starting materials are S_2O_7 or SO_2 and O_2 (fig. 2).

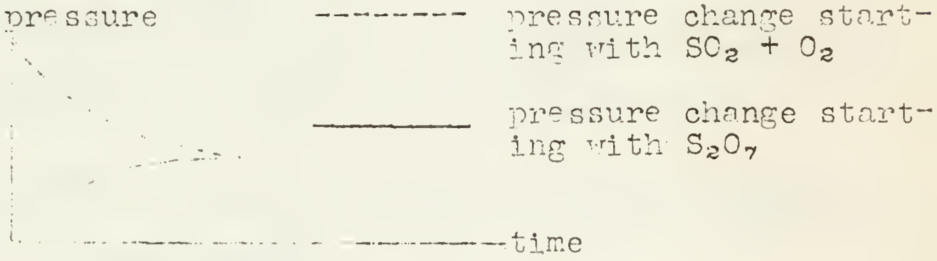


Figure 2

Analysis: This was carried out by titrating free iodine and H^+ after treatment of the substance with a KI solution:

$$(SO_3)_xO_{active} + 2I^- + (X-1)H_2O \rightarrow I_2 + XSO_4^= + 2(X-1)H^+$$

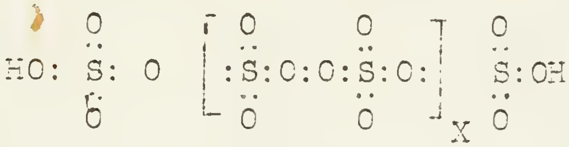
where X is the ratio between SO_3 and active oxygen. (For all peroxides the ratio $\frac{I+H^+}{S}$ should be 2). $SO_4^=$ was determined as $BaSO_4$.

In hydrolytic experiments the ratio $H_2SO_5:H_2S_2O_8:H_2SO_4$ was determined in presence of each other according to a special method devised by K. Gleu (12): Caro's acid is reduced by HBr and the bromine is absorbed in excess standard arsenite. Excess arsenite is determined by titration with standard potassium bromate. H_2O_2 is then titrated in the same solution with $KMnO_4$, the endpoint being determined by appearance of free bromine. Finally, $H_2S_2O_8$ is hydrolized by strong acid and Caro's acid and hydrogen peroxide determined as before.

Reactions of $(S_2O_7)_X$ 1) Concentrated H_2SO_4: Disulfur heptoxide does not dissolve in concentrated H_2SO_4, whereas SO_3, SO_4 and their mixtures(10) as well as the products prepared by Berthelot and Meyer dissolved readily. 2) Titanyl ions: Addition of an acid solution of titanyl sulfate to $(S_2O_7)_X$ gives an intensive orange colored ring(11). SO_4 does not give a titanyl peroxide reaction.(9)

3) Aniline: Aniline is completely oxidized to a tar by $(S_2O_7)_x$. SO_4 oxidizes aniline to nitrobenzene. 4) Mn(II): $MnSO_4$ is attacked only very slowly in presence of silver ions by $(S_2O_7)_x$ (at about the same rate as the slow conversion of $(S_2O_7)_x$ to Caro's acid). SO_4 oxidizes Mn^{++} instantaneously to MnO_4^- 5) Cu(II): $(S_2O_7)_x$ does not oxidize Cu(II) in alkaline solution to the alkali cuprate(III). It is claimed (9) that SO_4 brings about this oxidation. 6) $Cr_2O_7^=$: The dichromate ion is not oxidized by $(S_2O_7)_x$ 7) Water: $(S_2O_7)_x$ dissolves readily in cold water with some gas evolution (probably ozone) and formation of $H_2S_2O_8$, H_2SO_5 and a minor quantity of H_2SO_4 in solution.

Structural considerations: The proposed structure for $(S_2O_7)_x$ is:



$$\mathrm{HO{:}}\,\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{S}}}{:}\;\mathrm{O}\left[{:}\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{S}}}{:}\mathrm{O}{:}\mathrm{O}{:}\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{S}}}{:}\mathrm{O}{:}\right]_x\;\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{S}}}{:}\mathrm{OH}$$

This linear structure is supported by the following facts:
1) Hydrolysis gives $H_2S_2O_8$, H_2SO_5 and a little H_2SO_4. $(S_2O_7)_x$ is essentially the anhydride of $H_2S_2O_8$. 2) By increasing the amount of oxygen in the preparation of disulfur heptoxide a product containing a higher percentage of active oxygen (and consequently yielding upon hydrolysis a higher percentage of $H_2S_2O_8$) is obtained. It may be assumed that more S:O:O:S and fewer S:O:S bridges are formed.

A two dimensional sheet-like structure may also be considered ("This is consistent with the film-like nature of $(S_2O_7)_x$"-authors).

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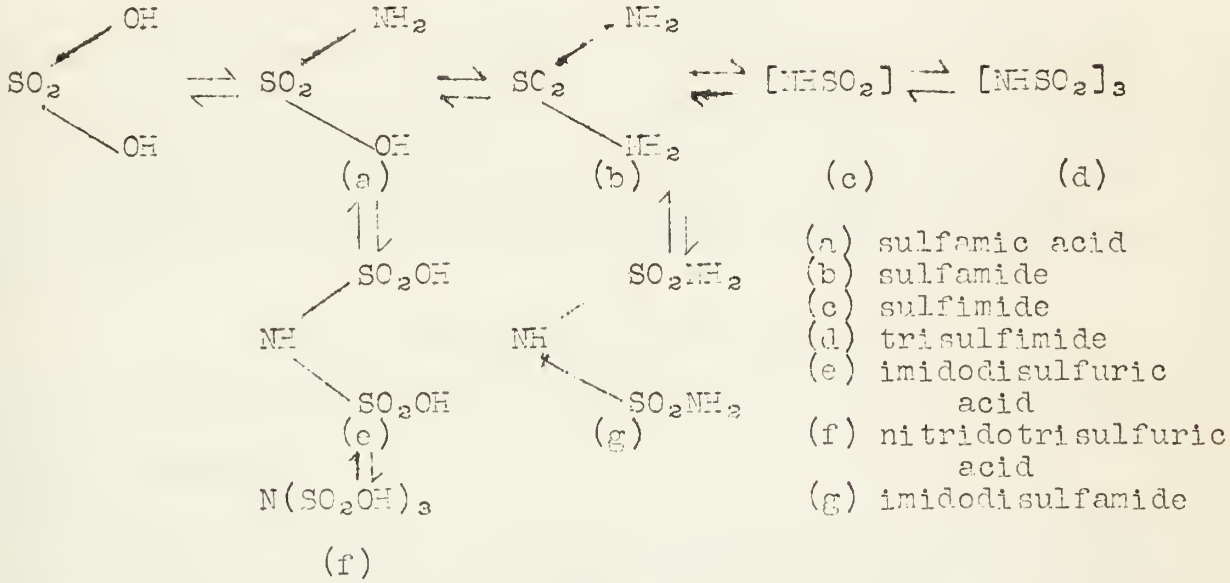
SULFANURIC CHLORIDE

L. H. Diamond April 21, 1953

INTRODUCTION:

Franklin[1] in his development of the nitrogen system of compounds set up the following tabulation of the nitrogen derivatives of sulfuric acid, or the aquo-ammono sulfuric acids:



(a) sulfamic acid
(b) sulfamide
(c) sulfimide
(d) trisulfimide
(e) imidodisulfuric acid
(f) nitridotrisulfuric acid
(g) imidodisulfamide

These relationships are somewhat formal and do not imply that the compounds are necessarily preparable from each other by the scheme outlined. Various aspects of the chemistry of the aquo-ammono sulfuric acids have been reviewed previously.[2,3] This report will consider the chemistry of trisulfimide, specifically the acid chloride of trisulfimide.

HISTORICAL:

Traube[4] isolated a number of salts from the reaction of sulfuryl chloride with ammonia. Analysis of the silver, sodium, potassium, and barium salts led him to believe that they were derived from sulfimide. Hantzsch and Holl[5] established that sulfimide did not exist as the simple momer, $[NHSO_2]$, but as the trimer $(NHSO_2)_3$. A ring structure was assigned to the compound based on its resemblance to cyanuric acid; the name sulfanuric acid has been suggested for the compound. Hantzsch and Holl claimed to have isolated free trisulfimide but later found that the product was an impure sample of imidodisulfamide.[6] Further attempts to prepare free trisulfimide have been unsuccessful. When sulfamide is heated above its melting point, the following reactions are postulated:

$$3SO_2(NH_2)_2 \longrightarrow (NHSO_2)_3 + 3NH_3$$

$$2SO_2(NH_2)_2 \dashrightarrow NH(SO_2NH_2)_2 + NH_3$$

It has been suggested that trisulfimide is formed from the decomposition of sulfamyl chloride, which may be an intermediate in the reaction of an aryl chlorosulfonate with ammonia.[7]

$$C_6H_5OSO_2Cl + NH_3 \longrightarrow NH_2SO_2Cl + C_6H_5OH$$
$$\downarrow$$
$$(SO_2NH)_3 + 3HCl$$

In an investigation of the reaction of phosgene with sodium amide Perret and Perrot noted the formation of melanuric acid and its chloride derivatives.[8] Because of the similarities existing between trisulfimide and melanuric acid, it seemed possible that trisulfimide may be obtained from the reaction of sulfuryl chloride and sodium amide. By fractional precipitation of the reaction products with silver nitrate, silver trisulfimide, $(SO_2NAg)_3$, was obtained. Hantzsch and Holl[2] prepared trimethyl trisulfimide in the following manner:

$$3CH_3I + (SO_2NAg)_3 \longrightarrow (SO_2NCH_3)_3$$

Tribenzoyl trisulfimide has also been prepared in a similar manner.

SULFANURIC CHLORIDE:

The reaction of sulfamic acid with phosphorous pentachloride was investigated by Ephraim and Gurewitch[9], who claimed to have isolated a binary compound of sulfamyl chloride, based on the following equation:

$$NH_2SO_2OH + 2PCl_5 \longrightarrow Cl_2 + HCl + POCl_3 + ClSO_2NH_2 \cdot PCl_3$$

Kirsanov[10] has shown recently that this reaction produces trichlorophosphazo sulfuryl chloride, according to the following equation:

$$NH_2SO_2OH + 2PCl_5 \longrightarrow 3HCl + POCl_3 + ClSO_2N{=}PCl_3$$

Trichlorophosphazo sulfuryl chloride is an extremely hygroscopic, white, crystalline compound; melting point at 35-36°. It is soluble in organic solvents and reacts with ammonia, amines, alcohol, and phenol. It hydrolyzes according to the equation:

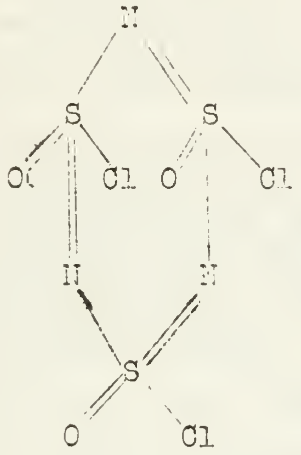
$$ClSO_2N{=}PCl_3 + 6H_2O \longrightarrow 4HCl + HOSO_2ONH_4 + H_3PO_4$$

Kirsanov[11] was able to prepare the sulfur analog of cyanuric acid, sulfanuric acid or 1-3-5trichloroxo-1-3-5 trithiatriazine, by the thermal cleavage of trichlorophosphazo sulfuryl chloride. The trichlorophosphazo sulfuryl chloride was distilled in vacuum and the residue obtained was a transparent brown liquid which contained the sulfanuric chloride. By fractional crystallization procedures, two products were obtained that corresponded to the formula $(NSOCl)_3$; these were designated by Kirsanov as α- and β-sulfanuric chloride. The α-sulfanuric chloride is a white crystalline product with a melting point of 144-145° and a boiling point of 270°; however, the

material explodes violently upon distillation. The β-sulfanuric chloride is also a white crystalline solid with a melting point of 42-43.

Sulfanuric chloride is soluble in ether and benzene; in alcohol the solution becomes acidic, probably involving the formation of esters of sulfanuric acid. Sulfanuric chloride reacts vigorously with ammonia, amines, and is slowly hydrolyzed by water.

Since sulfur in the hexavalent state, like carbon tends primarily to assume a tetrahydral configuration, sulfanuric chloride may exist as two geometric isomers, represented as the α and β forms.



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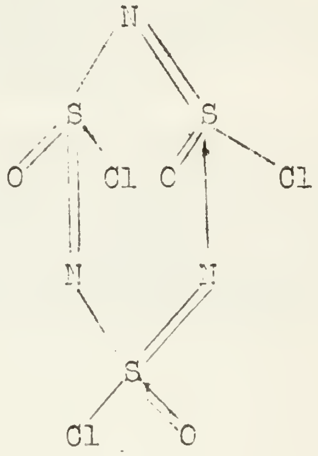

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ROLL CALL

THALLIUM TRIIODIDE

Robert H. Marshall April 21, 1953

Thallium triiodide was first prepared by Nicklès in 1864. Early methods of preparation involved the digestion of TlI and I_2 in ether, methanol, or ethanol solutions, followed by evaporation. A long period of digestion is necessary, however, owing to the low solubility of TlI and an intermediate iodide, Tl_3I_4. A better method has been reported by Sharpe, in which TlI is dissolved in a solution of I_2 in concentrated hydriodic acid(1). Evaporation at room temperature yields the TlI_3.

The isomorphism of TlI_3 with RbI_3 and CsI_3 appears to establish the structure of the solid as thallium (I) triiodide. However, the absorption spectrum in methanol solution shows different maxima than those characteristic of the I_3^- ion. When such a solution is treated with aqueous Na_2CO_3 solution, Tl_2O_3 is precipitated. This reaction may be considered to occur in the following stages:

$$\begin{array}{l}
2\ TlI_3 \rightleftharpoons 2Tl^+ + 2I_3^- \\
2\ I_3^- + 4OH^- \rightleftharpoons 2OI^- + 4I^- + 2H_2O \\
2\ Tl^+ + 2OH^- + 2OI^- + 2H_2O \rightleftharpoons 2Tl(OH)_3 + 2I^- \\
2\ Tl\ (OH)_3 \rightleftharpoons Tl_2O_3 + 3H_2O \\
\hline
2\ TlI_3 + 6OH^- \rightleftharpoons Tl_2O_3 + 6I^- + 3H_2O
\end{array}$$

As evidence for such a series of reactions, it has been found that when I_2 and alkali are added to a solution containing Tl^+ ions, Tl_2O_3 is precipitated quantitatively. In addition, KI_3 solutions are immediately decolorized by alkali.

Thermal decomposition of the TlI_3 yields TlI and I_2 as final products. X-ray powder photography has shown Tl_3I_4 to be an intermediate product. Experiments were also carried out which indicate the dissociation pressures of various polyhalides to be:

$$Tl_3I_4 < CsI_3 < RbI_3 < TlI_3 < KI_3.$$

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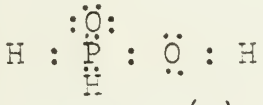
PREPARATION OF COPPER HYDRIDE IN AQUEOUS MEDIUM

N. E. Bojars April 28, 1953

A. INTRODUCTION.

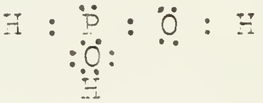
Hypophosphorous Acid as a Reducing Agent. Hypophosphorous acid reacts with copper (II) ions in water, yielding a red-brown reduction product. The constitution of this product has been the subject of controversy until recently. It has now been shown[1] that, under proper conditions, copper hydride (CuH) can be made in aqueous medium.

Several alkali salts of the monobasic hypophosphorous acid can be made from white phosphorus and the corresponding aqueous alkali.[2] A number of heavier metal salts has also been made.[3] The free acid can be prepared from barium hypophosphite and aqueous sulfuric acid,[4] or in resin exchangers.[5] Hypophosphorous acid is a colorless, crystalline compound, m.p. 26.5°C, readily soluble in water.[4] Two hydrogen atoms are attached to phosphorus (A).



$$H : \overset{:\ddot{O}:}{\underset{H}{\ddot{P}}} : \ddot{O} : H$$

(A)



$$H : \underset{\underset{H}{:\ddot{O}:}}{\ddot{P}} : \ddot{O} : H$$

(B)

Satisfactory proof has been advanced that a tautomer (B) does not exist[6-9]. However, two forms of the acid in a slow equilibrium with each other have been postulated[10,11] for aqueous solutions. The active reducing agent, according to Steele[12], is a hypothetical compound H_5PO_2, which is produced with measurable velocity. These assumptions are necessary to explain the rate of certain reactions,[13] where hypophosphorous acid is the reducing agent. The active form is produced, when the equilibrium amount is diminished [10,14]. Some objections against the current structural formulas for H_3PO_2 have been raised.[15] The ion $H_2PO_2^-$ is tetrahedral.[4] A study involving radioactive phosphorus has shown that mixtures of phosphates and hypophosphites do not exchange phosphorus, even upon heating to decomposition temperatures in closed vessels.[16]

Hypophosphorous acid is oxidized by many oxidizing agents and heavy metal ions[2,3,4,10,11]; in certain cases an induction period of the reaction is observed[17,18]. Hypophosphorous acid is useful for the production of nickel and nickel hydride alloys[19,20] via nickel hypophosphite, for electrode plating, and in ceramics, and as a stabilizer for iron (II) chloride[21]. The acid forms complexes with some metal ions.[22]

Hypophosphorous acid is a useful reducing agent in organic chemistry. A well-known example is the deamination,[23] involving the

replacement of the diazonium group by hydrogen. A method was found at the University of Illinois[24] for introducing deuterium into aromatic nuclei, in a similar way. The influence of various metal salts upon the deamination reaction has been studied and the mechanism has been discussed[25]. Hypophosphorous acid is also useful in the production of aryl phosphinic acids[26] and other organic compounds [27,28,29].

The use of the hypophosphorous acid in medicine[3] and biology[30], as a stabilizer for some polymers[31,32], and as a sensitizer for fumigating mixtures[33] can be mentioned.

B. The Reaction of Copper (II) Ions with Hypophosphite Ions.

It has long been known[34] that copper (II) ions are reduced by hypophosphite ions. Wurtz[35] obtained by such reduction a red-brown, amorphous precipitate, which he identified as copper hydride.

$$2\ Cu^{++} + 3\ H_2PO_2^- + 3\ H_2O \rightarrow 2\ \underline{CuH} + 3\ H_2PO_3^- + 4\ H^+ \qquad (I)$$

Copper hydride then decomposes with evolution of hydrogen.

$$2\ \underline{CuH} \rightarrow \underline{2\ Cu} + H_2 \qquad (II)$$

If excess of hypophosphite is present, hydrogen is evolved even during the initial stage of the reaction; with an excess of copper (II) salt copper only is precipitated[36,37]. The constitution of the product of the reaction (I) has been a subject of controversy[38] until recently. Thus, it has been maintained[2,36] that spontaneous decomposition and X-ray diffraction studies indicate that the product is a solution of hydrogen in copper as is the case with palladium, and that the red-brown precipitate is not a hydride analogous to the alkali hydrides.

The nature of metallic hydrides has been investigated recently[39] Wiberg and co-workers[40,41,42] have developed methods for the preparation of hydrides in non-aqueous media. Lithium aluminum hydride[43] was found to be useful for the preparation of dry copper hydride.

$4CuI + LiAlH_4 \rightarrow LiI + AlI_3 + 4\ CuH \qquad (III)$

Copper hydride can be dissolved in pyridine, and reprecipitated by ether. Thus it becomes evident that copper hydride is, after all, a definite chemical compound.

C. The Procedure for the Preparation of Copper Hydride in Aqueous Medium.

To obtain the desired results, the old method of Wurtz[35] was properly modified[1]. According to the equation (I), stoichiometric amounts of 0.4 M aqueous copper (II) sulfate and 0.6 M aqueous sodium hypophosphite containing 1.25% free sulfuric acid were allowed to react in a hydrogen atmosphere at 20°C for 15 to 20 hours. Precautior were made to exclude traces of oxygen, since otherwise some copper (I) oxide appears as an impurity in the product.

Wet copper hydride was precipitated; all attempts to dry it led a decomposition[1,44], even below 45°C. However, a satisfactory analys was obtained by a special procedure[1]. In more than 100 separate experiments a light red-brown product was always obtained[1]. It was shown by analysis to contain 98.45% Cu and 1.55% H, in excellent

agreement with the calculated values for CuH.

The earlier workers had obtained analytical values up to 1.50% H and about 98.50% Cu. An aqueous suspension of copper hydride has been shown to act as a reducing agent; an attempt to devise a quantitative titrimetric procedure has not been entirely successful because of difficulties in estimating the end point[1].

Thus it has been definitely proved[1] that copper hydride can be made in aqueous medium. Silver (I) ions yield silver metal only under similar conditions[36].

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INORGANIC PAPER CHROMATOGRAPHY

Mary Joan Sirotek May 5, 1953

HISTORY

Inorganic analyses on strips of absorbent paper were first described over a century ago. Weil and Williams (1) credit the first recorded experiments on capillary analyses to F. F. Runge, who in 1850 analyzed a mixture of dyes on blotting paper and whose interest extended to the possibility of using capillary ascent of solution in blocks of wood for the separation of solutes. At a later date this was more fully investigated by Schoenbein and his student, Goppelsroeder. Schoenbein, who has usually been regarded as the pioneer of capillary analysis of inorganic compounds, showed that if a strip of paper is dipped into water containing inorganic salts, the water rises in the paper and carries the salts with it. The solutes concentrated in distinct zones as the solution was drawn into the strip. He predicted its later use as an analytical tool (2). In 1878, Bayley (3) noted a similar phenomenon. Fischer (4) knew of this work and applied it to the quantitative investigation of the separation of sodium and barium, and of certain double salts. By separating the cations in a double salt, such as ferrous ammonium sulfate, he demonstrated the absence of a complex ion.

The true discovery of chromatography is credited to Tswett (5), who separated the pigments in leaves by passing a petroleum ether extract of leaves through a column of calcium carbonate. He named the method and stated, erroneously however, that it was based on purely physical reactions. Tswett vigorously denied that his work was related to the work of Schoenbein and Goppelsroeder.

In 1909, Krulla (6) recommended adsorption on filter paper as a simple qualitative test for salts which give a color reaction and as a measure of the concentrations of dilute solutions.

Chromatography was then nearly completely forgotten for almost 25 years. But lately much has been done to develop the usefulness of this tool.

Strain (7) has defined chromatography as the technique of analysis and/or preparation in which there is a dynamic partition or distribution of dissolved or dispersed materials between two immiscible phases, one of which is moving past the other.

PROCEDURE

Chromatographic separations may be run on either columns or paper strips.

The procedure for paper chromatography is essentially this: a spot of the solute to be analyzed is applied to one end of the paper and the developing solvent is made either to ascend or descend the paper, with the result that different solutes appear in different zones.

Many variations of this simple procedure have appeared using simple filter paper or blotting paper in the form of strips, disks, sheets, and piles. Consden et al (8) and Strain (9) have described a descending method. Williams and Kirby (10) and Rockland and Dunn (11) used an ascending procedure. Other variations of the method have been developed by Brown (12), Muller and Clegg (13), Rutter (14), Ma and Fontaine (15) and Datta et al (16). Attempts to apply paper chromatography to a larger scale have been made by Mitchell and Haskins (17), Porter (18) and Zanofsky et al (19).

Burstall and Kember (21) have given an excellent description of the practical problems involved in running a chromatogram. In general the following things must be considered:

a. The test solution
In general the concentration should be about 1 mg./0.05 ml. for a one inch wide strip.

b. Transfer of test solution to paper strip
For qualitative analysis, a 0.05 ml. pipet may be used. For quantitative analysis a micrometer syringe or capillary buret should be used. Novellie (21) has described a simple method of application.

c. Type and size of paper
A strip one inch wide and eight to sixteen inches long of Whatman No. 1 or 3 is usually satisfactory. Scribner and Wilson (22) have stated that paper cannot be considered inert even towards water and have set up standards for filter paper. Cassidy (23) has found that some paper gives bands due to the presence of copper. Different papers may even invert the order of the spots. The machine direction of the paper should also be considered. Flood (24) has used paper impregnated with alumina.

d. Atmospheric conditions
The chromatogram should be produced in a closed tank so that the atmosphere will be saturated with the vapor of the solvent to prevent evaporation.

e. Temperature
The temperature should be kept somewhat constant. Gordon (25) states that with rising temperature the adsorption decreased and the salt becomes more motile.

f. Time and distance of solvent movement
The time varies for fifteen minutes to thirty-six hours. For complete separation of a large group, the solvent front should move twelve inches. For some separations, two to three inches is sufficient.

g. Choice of solvent
The best method is to try one of each of the following types: alcohols, ketones, ether, carboxylic acids, esters, etc. When the best type has been found, different members of its homologous series are tried, usually with the addition of 1-2% mineral acid. The solvent is usually saturated with water. Lacourt et al (26) have shown the importance

of choosing the proper initial solvent.

h. Development and detection of zones
Physical methods include use of fluorescent indicators (27), photoelectric cells, interferometry, and radioactive tracers (28). Chemical methods may consist of spraying or streaking with a color producing reagent.

THEORY

A theory to be adequate should describe the formation and development of zones, their rate of movement, and their spatial as well as concentration dimensions. It should make it possible to calculate beforehand the state of development after a given amount of developer has been applied and should clarify the findings of experiment. Unfortunately the time has not arrived when a new substance can be placed on a paper, a developer added, and the results accurately predicted.

Many attempts have been made to develop a theory. Wilson (29) has devised a theory in terms of the adsorption isotherm which is used to express the relationship between solute and adsorbent at equilibrium. However, this does not take into account the effect of one solute upon another at varying concentrations. He neglects all diffusion and lack of equilibrium.

In 1941, Martin and Synge (30) introduced partition chromatography, in which the difference between partition coefficients in the aqueous and nonaqueous phases of the components of a mixture gave refinement in the normal chromatographic separation which depends upon adsorption characteristics. In 1944, Consden et al (8), extended this to the use of paper strips. Martin and Synge developed a plate theory for chromatography analogous to that used for distillation columns. They consider the column or strip to consist of a number of theoretical plates (H.E.T.P.) within each of which perfect equilibrium occurs and relate the partition coefficient to the rate of movement of the bands.

Thus, A = cross-sectional area of paper + nonmobile phase + mobile phase

A_L = cross-sectional area of mobile phase i.e., solvent phase

A_S = cross-sectional area of nonmobile phase i.e., water phase

$$\alpha = \text{partition coefficient} = \frac{\text{conc. in } H_2O \text{ phase}}{\text{conc. in solvent phase}}$$

$$R_f = \frac{\text{movement of band}}{\text{movement of advancing front of liquid}} = \frac{RA_L}{A} = \frac{A_L}{A_L + \alpha A_S}$$

$$\alpha = \frac{A_L}{R_f A_S} - \frac{A_L}{A_S} = \frac{A_L}{A_S}\left(\frac{1}{R_f} - 1\right)$$

Other attempts at development of a theory have been made. Flood (31) has related the zone radii to the concentration. Hopf (32) has developed Flood's formula further. Brimley (33) assumes that the spots spread by diffusion in a way analogous to the theory of heat flow. Thomas (34) discusses a theory of kinetics leading to a Langmuir type of isotherm at equilibrium.

However, no completely satisfactory theory has been devised.

MECHANISM

All chromatographic methods are based on the differential migration of solution through polyphase systems in which the phases have a preferential affinity for the solutes.

In considering the mechanism of chromatography, Arden, et al (35) have listed these factors as requiring consideration.

a. Selective extraction of the salts of the organic solvent, an effect prevailing at the test patch.

b. Where substantially immiscible solvents are used, partition of the inorganic substance between organic solvent and aqueous layer, since water is present as a normal constituent of the adsorbent paper and is usually added to the organic solvent. This partition therefore takes place as the liquid mixture moves down the paper, and separations are due to slight changes in conditions at different points on the adsorbent strip.

c. Adsorption of the metallic ions by the paper.

d. Formation of complexes with high solubilities in organic media under specific conditions.

Feigl (36) has compared the mechanism to a process of fractional precipitation. Muller and Clegg (37) have described the mechanism on circular filter paper. In the chromatographic field, it is often a moot question as to whether the separation is due to adsorption, ion exchange, liquid-liquid distribution or a combination of two or three of these. The predominant force varies with the solvents and the solute. Thus, Pollard, et al (27) state that for butanol mixtures in cation analysis the separation is essentially partition chromatography whereas in collidine, complex formation and selective extraction play the dominant role.

APPLICATIONS

The most obvious application of paper chromatography is the qualitative detection of substances. Although most of the ground work has been done with amino acids, recently applications to the detection of cations and anions have become more abundant. Lederer (38) has devised a method for the separation of the noble metals. Arden et al. (35) have found a method for the separation of several metal ion groups, namely, Ca Sr Ba; Al Ga In Zn; Co Cu Fe Mn Ni; and Pb Cu Bi Cd Hg. A more intensive investigation by Pollard, et al (39) has resulted in a scheme for the separation of Pb, Ag, Hg, As, Sb, Cr, Mn, Cu, Co, Ni, Bi, Fe, Sn, Sr, Ba, Cd, Zn, Al, Mg, Ca, Na, and K. Later Pollard, et al (40) extended the scheme to include Ce, Li, Mo, Tl, Ti, U, V, and W. Anion analysis has developed more slowly, but Lederer (41) has devised a scheme for the separation of the chloride group anions. Fillinger (42) has devised a simple scheme to be used in elementary qualitative analysis. She makes use of alumina columns but the procedure could also be applied to paper.

A method of two dimensional chromatography has been discussed by Consden (43) and Tolley (44). The "maps" produced by this method can be used for identification of more difficult substances since two solvents may be used.

Methods for quantitative analysis have developed more slowly. For semi-quantitative work, the stain is compared with those made by known amounts of substance. For more accurate work, the color band is cut out and the metal content determined accurately by colorimetric, polarographic, and spectographic techniques. Fischer (45) has described several simple methods for the quantitative assay of amino acids. This method is applicable to other problems. Bull et al. have plotted the % transmission on semi log paper versus the distance along the strip and by means of a planimeter have estimated the concentration of amino acids.

Anderson and Lederer (47) have combined quantitative analysis with electrochromatography on paper. Strain (48) has used two and three way electrochromatography for the resolution of mixtures.

An application for the determination of molecular structure has been described by Strain (9). He has done this work by studying the adsorption sequences and relative rates of migration. Strain (7) has also studied the effect of ionic charge, radius and mass on the degree of separability.

ADVANTAGES AND DISADVANTAGES

Some of the advantages of paper chromatography include its use for the separation of substances too unstable to be distilled, the concentration of dilute solutions, and the determination of the purity, homogeneity, and components of solutions. It is also a rapid, simple, and inexpensive method.

Unfortunately, at the present time there is a considerable degree of empiricism involved in chromatography. There is a great deal of physical data to be worked out. Paper chromatography is not applicable to large scale work. There is always the chance of chemical change in the adsorbed solute.

Because there is some confusion in nomenclature, Dent (49) has recommended the use of the word "papyrography" as a substitute for paper chromatography, but his suggestion has not been carried out very widely.

Much work remains to be done in this subject, especially in the way of further quantitative studies of its physico-chemical nature, including kinetic studies so as to evaluate the various factors involved in a more quantitative and predictable fashion.

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INORGANIC COLUMN CHROMATOGRAPHY

S. A. Bartkiewicz May 12, 1953

Chromatography, a simple and ingenious method of chemical analysis by adsorption, was invented in 1906 by M. Tswett, a Russian botanist, while working with plant pigments. The method was used sporadically in biological research; but, it was almost thirty years later before chromatography found any serious application in the inorganic field. (24,27,33) It has been used in inorganic chemistry chiefly for the resolution and identification of mixtures of cations. Chromatography has also been applied to some extent in the separation of elements, detection of anions, purification of inorganic compounds, and the separation of isotopes. Some attempts have been made to apply this method quantitatively.

Strain (24) describes the mechanism of chromatography as a dynamic process which depends upon the continuous and simultaneous adsorption, desorption, or elution and readsorption of the substances being resolved upon the column. Concepts regarding the details of the adsorption process itself are not entirely clear. (16,19,28,34) In adsorption columns several types of adsorptive forces may come into play. These may be of the physical type, Van der Waal's forces, or ential chemical reaction, chemadsorption.

The choice of column size, adsorbent and solvent, is determined to a large extent by the quantity and the adsorbability of the materials to be resolved, the physical and chemical nature of the adsorbent, the solubility of the materials to be adsorbed, and by the activity and solubility of the adsorbent. (16,19,27,30) Final selection is usually, however, made by empirical methods. (27) Le Rosen (37) attempted to standardize chromatography, and suggested a method for determining the characteristics of an adsorbent which would aid researchers in reproducing the work of other people.

Terminology indicates limitation to colored substances only. Modification of the process and the procedure, however, makes it possible to work with colorless materials and to locate colorless bands. (9,27)

It should be kept in mind that most of the above material has been derived and postulated with reference primarily to organic materials. Much of it undoubtedly does apply to inorganic materials as well.

The first extensive work done in inorganic chromatography was by Schwab and Jockers. (19) They examined a variety of substances which could be used as adsorbents and used several of the standard reagents for developers. Using Al_2O_3 as an adsorbent and primarily H_2S and $(NH_4)_2S$ as developers, they obtained a definite series order of adsorption for a number of cations. Working with Dattler (20,21) Schwab found that by treating Al_2O_3 with HNO_3 an anionic series could be obtained--the cations being used as developers. An endeavor was made to arrive at the quantitative possibilities of chromatography by attempting to correlate band widths with concentration of the ion. Srikantan and Krishman (25) applied the method to the quantitative

determination of various constituents of alloys such as brass and steel. They report that 99% accuracy can be obtained by careful control of the method. Kubli (17) investigated the work of Schwab and Dattler (20) with anions and extended the series order to almost twice its original number. Schwab and Ghosh (22) investigated the possibilities of the application of chromatography to qualitative analysis. Some success was obtained with the HCl, H_2S and $(NH_4)_2S$ groups. Bishop recommends the use of chromatography in teaching qualitative analysis and cites two examples that can be used. Fillinger and Troftan (15) have reported the successful application of chromatography to some degree in undergraduate qualitative analysis at Hollins College, Virginia. Schwab and Ghosh (23) investigated the use of chromatography in micro analysis and found that the sensitiveness of the method is as great and in some cases greater than by the drop method. They also made separations of the noble metals, using Al_2O_3 as an adsorbent. No developers were required since the compounds used were themselves colored. Tanaka and co-workers (29) found that the presence of .001γCo, 0.001γ of Ni, 0.001γ of Zn, and 0.5γ of Cu could be determined using an Al_2O_3 column and $(NH_4)_2S$ as a developer. Venturello and Saini (32) report the separation of the Pt group upon Al_2O_3 using various developers. Venturello and Agliardi (31) investigated the work of Schwab and Jockers (19) and further extended the cationic series. Erlenmeyer and co-workers also extensively investigated the use of chromatography in inorganic analysis. Using 8-hydroxyquinoline as the adsorbent Erlenmeyer and Dahn (12) succeeded in resolving a series of ions. No developer was needed since the oxime itself served the purpose. Working with Violuric acid as an adsorbent, Erlenmeyer and Schoenauer (14) were successful in separating Na^+, and K^+ as well as most of the alkaline earths. Erlenmeyer and Schmidlin (13) extended the work upon the Na-group. Robinson (33) working with a mixture of starch and 8-hydroxyquinoline further extended the series order of Erlenmeyer and Dahn. He also successfully determined the Zn content of Cu - Ni brazing alloys by the method of band width measurements. Dean (10) using a combination of chromatography and colorimetry successfully isolated and determined Cobalt in ferrous and non-ferrous alloys. Several successful separations of ions have been reported using cellulose as an adsorbent. (4,6,7,8,34) Kutzelnigg (18) using ZnS as an adsorbent successfully obtained the following series order: Au, Os, Ru, Pd, Hg, Ag, Bi, Cu, Fe, U, Pt, Rh, and Ir. The formation of sulfides produced sharply defined zones which can be identified by their color. Traces of Ni have been determined by the use of D.M.G. as an adsorbent. (5) Metals in the form of dithizone complexes have been separated upon an Al_2O_3 column by Bagh (2) and by Dunabin. (11) Al-Mahdi and Wilson (1) have resolved Co^{+2}, Cu^{+2}, Fe^{+3}, and Ni^{+2} as diethyldithiocarbamates.

Work in this field is still fragmentary due to the lack of proper adsorbents. (16) With the development of a more universal adsorbent, a complete scheme of analysis, qualitatively and possibly quantitatively, will probably be conceived.

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AMMONOLYSIS AND AMINOLYSIS OF SOME SUBSTITUTED SILICON HALIDES

A. S. Hay May 19, 1953

In general the halosilanes are uniformly more reactive than their carbon analogs[1]. Trichlorosilane and tetrachlorosilane are hydrolyzed even by moist air. As the halogen atoms are replaced by alkyl or aryl groups the ease of hydrolysis decreases[2,3] and the stability also increases as bulkier groups are put into the molecule[4]. With increasing bond polarizability the ease of hydrolysis also increases in the order F, Cl, Br, I.

All of the halosilanes (with the exception of the fluoro compounds) react with ammonia at room temperature, or with liquid ammonia[5]. In this manner the silicon analogs of primary and secondary amines can be prepared[6,7]. Miner et al[8] treated t-alkoxychlorosilanes with ammonia and found that the type of product resulting from the reaction depended on the ratio of chlorines to silicon in the molecule The mono- and dichlorosilanes formed the corresponding mono- and diaminosilanes, but the trichlorosilanes reacted with ammonia to give only resinous condensation products. Trisilylamine, prepared from tetrachlorosilane and ammonia, is the only known analog of a tertiary amine. They also found that the presence of at least one tertiary alkoxy group in the molecule is essential for the existence of a stable compound containing two amino groups on the same silicon atom.

In contact with water these t-alkoxyaminositanes react rapidly with evolution of ammonia to give silanols. They also react rapidly with most primary and secondary alcohols at room temperature with the evolution of one mole of ammonia.

$$(RO)_2Si(NH_2)_2 + R^1OH \rightarrow (RO)_2(R^1O)SiNH_2 + NH_3$$

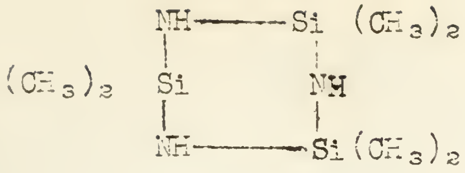
With methanol both amino groups react readily but heat is needed for the reaction with higher alcohols. At elevated temperatures with primary alcohols the second amino group reacts readily, with secondary alcohols the reaction is slower, and with tertiary alcohols the first amino group reacts slowly and the second not at all.

Generally trialkylchlorosilanes react with ammonia to give the corresponding disilazanes but triethylchlorosilane is reported to give some triethylaminosilane also.

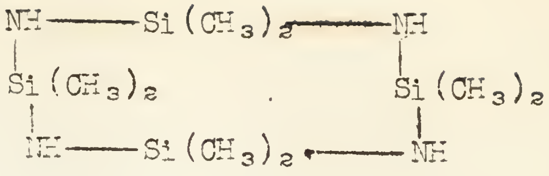
Similarly the reaction of tetrachlorosilane with alkylamines yields the corresponding N-alkyldisilazanes. Trimethylchlorosilane and methylamine react to form trimethyl-N-methylaminosilane. Reaction with a further molecule of trimethylchlorosilane gives heptamethyldisilazane.

$$(CH_3)_3SiCl + CH_3NH_2 \rightarrow (CH_3)_3SiNHCH_3 \rightarrow [(CH_3)_3Si]_2NCH_3$$

By reaction of ammonia with dimethyldichlorosilane Larsson and Smith[9] obtained hexamethylcyclotrisilazane (I) and octamethylcyclotetrasilazane (II). Both are hydrolyzed by water.



I



II

Dimethyldichlorosilane and methylamine or ethylamine in a 1:4 ratio yield as the main products dimethyl-bis-(methylamino)-silane and dimethyl-bis-(ethylamino)-silane, respectively.

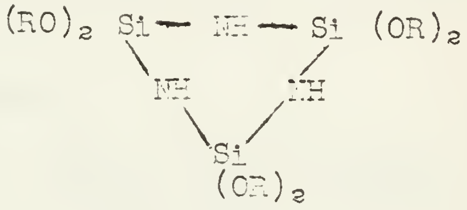
$$4RNH_2+(CH_3)_2SiCl_2 \rightarrow (CH_3)_2Si(NHR)_2+2RNH_3Cl$$

Schwarz and Weigel[10] prepared some aminosilanes and studied their conversion to the disilazanes. They prepared triisopropoxyaminosilane by introducing dry ammonia into an ether solution of triisopropoxychlorosilane. It is very sensitive to moisture. When heated under reflux, ammonia is evolved and after 48 hours a 50 percent yield of the disilazane was obtained. When triphenoxyaminosilane, prepared in a similar manner, is heated it is converted quantitatively to the disilazane.

The preparation of diisopropoxydiaminosilane was attempted in a manner analogous to that for the monoaminosilanes. It could not be prepared but instead a mixture of tetraisopropoxydisilazane(III) and hexaisopropoxycyclotrisilazane(IV) was obtained. In order to determine whether the cyclic compound was formed by a further condensation of

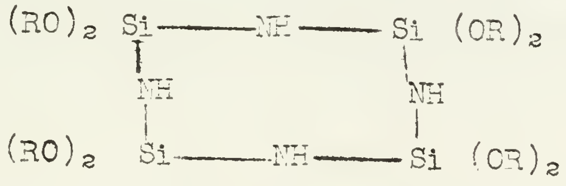
$[(RO)_2Si]_2NH$

III



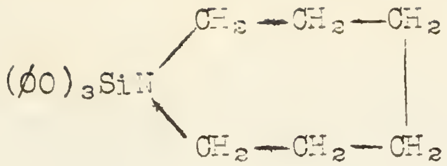
IV

the disilazane, some of the latter was heated for some time at 180 deg. Under these conditions a mixture of the cyclotrisilazane(IV) and cyclotetrasilazane(V) was obtained. These compounds, as all other aminosilanes are sensitive to water, ammonia being split out.



V

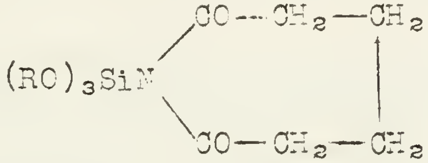
Triphenoxychlorosilane and hexamethylenediamine react in methylene chloride at the boiling point to give a mixture of triphenoxyaminosilane and triphenoxyhexamethyleniminosilane(VI). After six days



VI

in a desiccator over phosphorus pentoxide the cyclic compound crystallized out of the mixture. In contrast to other aminosilanes and disilazanes described, it is comparatively stable to moisture. Several hours in contact with water at room temperature produces only a slight amount of hydrolysis.

In an attempt to prepare a molecule containing the grouping -SiNHCO- four moles of triisopropoxyaminosilane and one mole of adipoyl chloride were condensed in refluxing ether solution. A mixture of triisopropoxyadipimidosilane (VII) and hexaisopropoxydisilazane was obtained. The cyclic compound could be purified by crystallization from benzene. It is extraordinarily susceptible to hydrolysis and gives by reaction with water, ammonia, adipic acid, and hexaisopropoxydisilazane which undergoes further hydrolysis to yield hexaisopropoxydisiloxane.



VII (R = $(CH_3)_2CHO-$)

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Thesis Report

Niels C. Nielsen May 26, 1953

The preparation and study of the structures and properties of some metal derivatives of azo and azomethine dyes has led to interesting results with respect to the theoretical aspects of coordination chemistry and may well be of practical value to the dye industry which has used these "lakes" for many years. One aspect of this problem concerns the donor properties of the azo group.

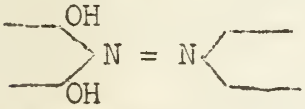
The earlier characterization of the metal lakes of azo dyes as Werner-type coordination compounds was accomplished by Morgan and Drew, and their associates and students, who prepared, analyzed, and performed various substitution reactions on these compounds. This work showed the necessity of having substituents such as -OH, NH_2, etc. in at least one position ortho to the azo group in order to form stable complexes. The later workers also indicated that the azo group was involved in the formation of only one coordinate covalent bond.[1]

Callis and Nielsen[2,3] continued this investigation and, by the use of magnetic susceptibility measurements, was able to establish the configuration of a large number of complexes. Further work by Liu[4] and the measurement of stability constants by Snavely and Fernelius[5] permits a rather complete evaluation of the metal complexes of the azo dyes.

With respect to the azo group as a donor, Feigl[6] has found it possible to induce color changes in solutions of azo dye indicators by the addition of $Pd(CN)_2$. The dyes used did not contain any ortho substituents, and the change, apparently, cannot be produced by any other compound.

Since the azo group does contain enough atoms to furnish two pairs of electrons, in addition to π electrons from the double bond, it may be possible to form two coordinate covalent bonds with this group. In examining the absorption spectra of various dyes and their metal complexes in neutral, acid, and alkaline solution, some evidence has been found for the addition of a proton to the azo group without completely rupturing the coordinate bond previously established with a metal ion. The resulting spectra are also being evaluated with respect to the affect of chemical constitution on the color of these compounds.

In an effort to induce the azo group to form more than one bond, the following dyes are being prepared:



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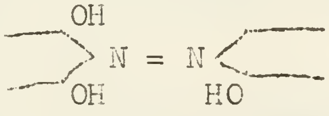

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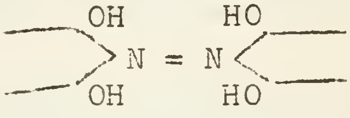

A study of the metal complexes of these dyes should provide some clarification of the donor properties of the azo group.

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THESIS REPORT

The Synthesis of Hydrazine

Roger W. Sanftner May 26, 1953

Interest in an economic synthesis of hydrazine has been heightened of late by the use of hydrazine as a speciality fuel. Furthermore many uses, e.g. in polymers or agricultural chemicals, for substantial quantities of hydrazine are conceivable should a low cost procedure for manufacture of hydrazine be developed. Many approaches have been devised, but the Raschig synthesis (1), modified but slightly, still remains the principal technical process in operation in this country today.

Recently Mattair and Sisler (2) reported the isolation of hydrazine from the interaction of gaseous chlorine with liquid and gaseous ammonia. They stated that the yield of hydrazine is dependent upon the ammonia to chlorine ratio and upon the ammonium chloride concentration. Wiberg and Schmidt (3) report that chloramine and ammonia dissolved in anhydrous ether give no hydrazine whereas, with water present, hydrazine was reported to have been formed.

A study has been undertaken of the reaction of ethereal solutions of chloramine with liquid ammonia under various conditions in order to determine the effect of ammonium chloride on the ammonolytic reaction of chloramine and liqiid ammonia. The reaction between hydrazine and chloramine in liquid ammonia was also investigated.

McElroy (4) and Oldham (5) have found that chloramine will undergo an one electron reduction at the dropping mercury electrode in liquid ammonia. Hydrazine could be postulated as one of the products of such a reaction. Since chloramine undergoes such a reduction, it was suggested that chemical reduction of chloramine might result in the formation of hydrazine. The reaction of aqueous chloramine solutions with a variety of amalgams was investigated; it was found that under certain conditions small quantities of hydrazine are formed.

In Raschig's original work, a variety of mateials was investigated in an attempt to find a substance which would act as a catalyst for the reaction between hypochlorite and ammonia. It was found that glue and gelatin are effective in increasing the yields of hydrazine; it was first assumed that the increased viscosity of the solution served to in-

crease the yield. Subsequent investigations by Bodenstein (6,7) and Møeller (8) have shown this theory to be incorrect. These investigations have shown that the presence of small amounts of metallic ions catalize the decompositon of hydrazine during the course of the reaction; glue and gelatin serve as metallic deactivators. Many substances have been investigated as substitutes for glue and gelatin (1,9.10). These two materials still remain, however, the most satisfactory substances from the standpoint of yield. None the less many disadvantages arise from their use. An investigation was begun to determine the role of gelatin in its removal of metallic ions from solution and also to discover an effective agent which would not posses the disadvantages exhibited by gelatin. Many substances have been investigated and several promising alternative materials have been found. Furthermore, it is believed that the cause of effectiveness of gelatin has been found.

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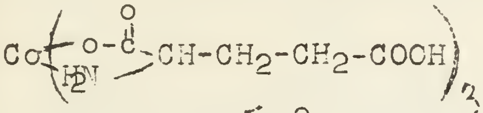
P.A.HORRIGAN May 26,1953

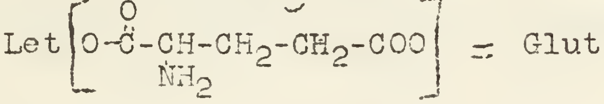
A Study of the Uncoordinated Carboxyl Groups in Glutamic Acid Complexes

There have been reports that uncoordinated functional groups on ligands react one way when the ligand is coordinated to a metal atom, and another when the ligand is "free".[1,2]

It was decided to prepare complexes of cobalt and copper with glutamic acid and study the properties of the uncoordinated carboxyl groups. The following compounds were prepared:

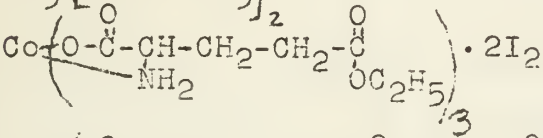


$Co\left(O-\overset{O}{C}-CH(H_2N)-CH_2-CH_2-COOH\right)_3$

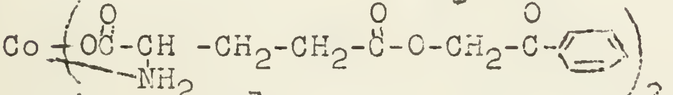


$\text{Let}\left[O-\overset{O}{C}-\underset{NH_2}{CH}-CH_2-CH_2-COO\right] = \text{Glut}$

$Na_3[Co(Glut)_3]$
$Ag_3[Co(Glut)_3]$
$Co_3[Co(Glut)_3]_2$

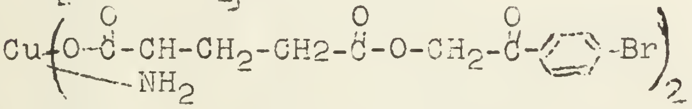


$Co\left(O-\overset{O}{C}-\underset{NH_2}{CH}-CH_2-CH_2-\overset{O}{C}-OC_2H_5\right)_3\cdot 2I_2$



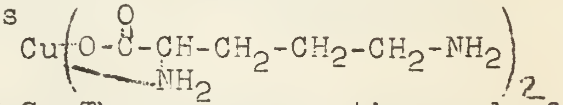
$Co\left(O\overset{O}{C}-\underset{NH_2}{CH}-CH_2-CH_2-\overset{O}{C}-O-CH_2-\overset{O}{C}-C_6H_5\right)_3$

$Na_2[Cu(Glut)_2]$
$Cu[Cu(Glut)_2]$



$Cu\left(O-\overset{O}{C}-\underset{NH_2}{CH}-CH_2-CH_2-\overset{O}{C}-O-CH_2-\overset{O}{C}-C_6H_4-Br\right)_2$

As an extension of this study, the application of the "masking effect" is being attempted with some of these complexes. The "masking effect" was first illustrated by A.C.Kurtz[3,4], who prepared amino derivatives of such complexes as



$Cu\left(O-\overset{O}{C}-\underset{NH_2}{CH}-CH_2-CH_2-CH_2-NH_2\right)_2$

and, who then removed the metal with H_2S. Thus, one reactive end of the molecule was "masked" while the other was left free to form a derivative. The phenacyl derivatives mentioned above are being treated to yield the metal-free ligands.

This work has shown that the uncoordinated carboxyl groups in cobalt and copper glutamate complexes exhibit no anomalous properties.

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Journal of Physical Chemistry (J. Phys. Chem.);
Analytical Chemistry (Anal. Chem.);
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Journal of the Electrochemical Society (J. Electrochem. Soc.);
Journal of the Chemical Society (J. Chem. Soc.);
Nature (Nature);
Science (Science);
Transactions of the Faraday Society (Trans. Faraday Soc.);
Proceedings of the Royal Society of London (Trans. Royal Soc. London);
Journal of Chemical Physics (J. Chem. Phys.);

Zeitschrift für anorganische Chemie (Z. anorg. Chem. or Z. anorg. allgem. Chem.);
Angewandte Chemie (Angew. Chem.):
Chemische Berichte (Chem. Ber. or Ber.);
Comptes rendus (Compt. rend.);
Helvetica Chimica Acta (Helv. Chim. Acta)

3. Review:

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